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BIODEGRADATION OF PROPYLENE GLYCOL-BASED MIL-A-8243D AIRCRAFT DEICER

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Biological degradation of propylene glycol in propylene glycol-based Mil-A-8243D aircraft deicer was investigated under conditions designed to simulate degradation in the environment. Shake flask, static flask, and static culture tube experiments were conducted using water from Westover Air Force Reserve Base (AFRB) and Buckley Air National Guard Base (ANGB). Degradation in water from Westover AFRB was limited by phosphorous availability. Phosphorous from the phosphate buffer in the deicer accelerated degradation relative to pure propylene glycol. Degradation in flasks receiving supplemental nitrogen and phosphorous was rapid, and propylene glycol depleted within 6 days. Water from Buckley ANGB was more limited in nitrogen than phosphorous, and propylene glycol degradation for both deicer and pure propylene glycol was slow. Addition of supplemental nitrogen in the form of ammonia resulted in markedly higher degradation rates. Additional information on contaminant levels in and characteristics of runoff is needed to support future research. Information on the additives in commercial deicers, which is usually proprietary, is needed for evaluating potential environmental impacts and performing any needed research. Additional research on metabolites and intermediates of propylene glycol degradation would be particularly indicated if difficulties are encountered in reducing DOD and COD to acceptable levels in treatment facilities. The production of metabolytes during environmental degradation of propylene glycol should be verified as part of field studies.

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PREFACE

This report was prepared by Capt William Gooden, Department of Chemical and Bioresource Engineering, 100 Glover Hall, Colorado State University, Ft. Collins, CO 80523 in partial fulfillment of requirements for an M.S. degree in Chemical Engineering specializing in Environmental Engineering.

This technical report presents the results of laboratory studies designed to simulate degradation of propylene glycol based Mil-A-8243D aircraft deicer in water and soil from Buckley ANGB and Westover AFRB. Propylene glycol degradation and metabolite / intermediate production are presented and discussed. Results of a sodium tolytriazole partition coefficient study are also presented and discussed.

The author expresses his appreciation to Dr. Kenneth Reardon, Dr. Vincent Murphy and Dr. James Linden for the advice and guidance they provided.

The work was performed between June 1995 and June 1997. The AL/EQM program manager was Capt Dennis O'Sullivan.

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EXECUTIVE SUMMARY

Runoff from aircraft deicing operations is covered by the EPA Stormwater regulations and state/local environmental regulations. Possible environmental impacts include oxygen depletion in receiving waters, aquatic toxicity of additives, and contribution to oxygen demand and phosphorous pollutant loadings.

Biological degradation of propylene glycol in propylene glycol-based Mil-A-8243 aircraft deicer was investigated under conditions designed to simulate degradation in the environment. Shake flask, static flask and static culture tube experiments were conducted using water from Westover AFRB and Buckley ANGB.

Propylene glycol degradation rates were limited by the availability of nitrogen and phosphorous in the water. Degradation in water from Westover AFRB was limited by phosphorous availability. Phosphorous from the phosphate buffer in the deicer accelerated degradation relative to pure propylene glycol. A 2 day lag phase was followed by a phase of rapid cell growth and substrate consumption during which propylene glycol disappeared at rates of 76-83 mg/L/day. Propylene glycol disappearance during the final, nutrient limited phase, was 20-25 mg/L/day. Degradation in flasks receiving supplemental nitrogen and phosphorous was rapid, and propylene glycol was depleted within 6 days.

Water from Buckley ANGB was more limited in nitrogen than phosphorous, and propylene glycol degradation for both deicer and pure propylene glycol was slow. Flasks with initial concentrations of 350 mg/L of propylene glycol exhibited a 2-4 day lag time followed by degradation rates of 10-12 mg/L/day. Addition of supplemental nitrogen in the form of ammonia resulted in markedly higher degradation rates.

The surfactant and flame retardant did not have significant effects on propylene glycol degradation rates. Disappearance of tolytriazole from a shake flask spiked with tolytriazole coincided with propylene glycol degradation. Results of this test need to be confirmed by further experimentation.

1-Hydroxy, 2-propanone was identified by gas chromatography as the major intermediate of aerobic degradation of propylene glycol. The 1-hydroxy, 2-propanone peak was split in the chromatograms indicating that a second compound was probably present. Hydroxy propanone was not persistent and disappeared before or within 1-2 days after depletion of propylene glycol. Propionaldehyde, n-propanol, propanoic acid, and an unidentified compound were the major metabolites in anoxic/anaerobic degradation of propylene glycol in nutrient supplemented water from Buckley ANGB. Anecdotal reports of objectionable odors are probably due to propionaldehyde. Another possibility is production of hydrogen sulfide and mercaptans. Metabolites and intermediates observed were in agreement with previous pure culture studies except that a major metabolite corresponding to the unidentified compound was not reported in literature.

The relationship between temperature and degradation rates determined in this study is considered unreliable due to uncertainties in degradation rates and because the microbial population may have changed between the start of the 20°C experiments and the 10°C

experiments. Continuous stirred tank reactor (CSTR) experiments should be considered for any future studies on the relationship between degradation rates and temperature.

Aquatic toxicity tests showed that propylene glycol and metabolites of propylene glycol were not acutely toxic to *Ceriodaphnia dubia*. The surfactant, sodium di-(2-ethylhexyl) sulfosuccinate, and the flame inhibitor, sodium tolytriazole, were more toxic than propylene glycol and metabolites of propylene glycol degradation.

Microbial concentrations and populations and the chemical and physical characteristics of runoff water are expected to be highly variable. In most instances, the potential for oxygen depletion should be mitigated by environmental conditions. In phosphorous limited waters, the phosphate buffer in Mil-A-8243D aircraft deicer could provide sufficient phosphorous to promote rapid biological degradation that could deplete dissolved oxygen.

The work of Pillard and aquatic toxicity data for tolytriazole have demonstrated the potential for aquatic toxicity of deicer additives. Since the potential for oxygen depletion will often be mitigated by environmental conditions as discussed above, aquatic toxicity will be the major acute effect of concern in most situations.

Additional information on contaminant levels in and characteristics of runoff is needed to support future research. Information on the additives in commercial deicers, which is usually proprietary, is needed for evaluating potential environmental impacts and performing any needed research.

Additional research on metabolites and intermediates of propylene glycol degradation may be warranted. Additional research in this area would be particularly indicated if difficulties are encountered in reducing BOD and COD to acceptable levels in treatment facilities. The production of metabolites during environmental degradation of propylene glycol should be verified as part of field studies. The presence of metabolites can, potentially, be used as an indicator that biological degradation of propylene glycol is occurring. The presence of propionaldehyde and/or n-propanol, which are both easily detectable by gas chromatography, would indicate anaerobic degradation and oxygen depletion.

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INTRODUCTION

A. Overview

Runoff from aircraft deicing operations has been receiving increasing attention. The runoff is covered by the EPA Stormwater regulations and state/local environmental regulations. Possible environmental impacts include oxygen depletion in receiving waters, aquatic toxicity of additives, and contribution to oxygen demand and phosphorous pollutant loadings. Glycol from aircraft deicing has also been found in groundwater next to airports on a seasonal basis.

Biodegradation of various glycols in the environment has been investigated, but most published studies have not considered additives present in aircraft deicers, and ethylene glycol has received more attention than propylene glycol. HQ AFRES/CEV submitted a research need on the fate of deicing chemicals in the environment.

B. Objective

The objectives of this effort were to: (1) investigate biological degradation of propylene glycol in propylene glycol-based, Mil-A-8243D aircraft deicer under laboratory conditions designed to simulate degradation in the environment; (2) determine rates of degradation and the effects of temperature, deicer additives, nutrients and dissolved oxygen on degradation; and (3) assess the practical importance of metabolic products and intermediates in the biological degradation of Mil-A-8243D aircraft deicer.

C. Scope

Biological degradation of propylene glycol-based, Mil-A-8243D aircraft deicer was investigated in the laboratory under conditions designed to simulate degradation in the environment. Runoff and soil from two bases, Westover AFRB, MA and Buckley ANGB, CO were used as inoculum for the studies.

D. Background

1. Use of Glycol Aircraft Deicers

Ice and frost are removed from aircraft by spraying with deicing fluid heated to 180-200°F. The heat melts the ice or frost. Ethylene or propylene glycol depresses the deicer freezing point and prevents refreezing. Of the deicer sprayed on the plane, between 49 and 80 per cent falls on the apron with the remainder staying on the plane or being dispersed in the air. (1) Ethylene/propylene glycol levels ranging from near zero to 19,000 mg/L have been found in runoff from commercial airports. (1)

2. Composition of Aircraft Deicers

a. Mil-A-8243D Aircraft Deicer

Type I military aircraft deicer is an unthickened, propylene glycol based deicing fluid. Type II military aircraft deicer, which is being phased out, is an unthickened ethylene glycol based deicing fluid. There is no military specification for thickened aircraft deicers. The composition of Type I, propylene glycol deicer as given in Mil-A-8243D is shown in Table 1.

Table 1. Composition of Propylene Glycol Based Mil-A-8243D Aircraft Deicer

Component	Weight %
Propylene glycol (1,2 Propanediol)	88.0 minimum
Water	9.0-10.0
Dibasic potassium phosphate (K_2HPO_4)	0.9-1.0
Sodium di-(2-ethylhexyl) sulfosuccinate (100% active)	0.45-0.55
Sodium salt of tolytriazole	0.50-0.60

b. Additives:

The sodium salt of tolytriazole is added as a flame retardant. The structure for tolytriazole is shown in figure 1. Isomerization is not controlled in the manufacture of commercial tolytriazole. Tolytriazole is also used as a corrosion inhibitor for metal parts storage and shipping applications, antifreeze formulations, hydraulic/brake fluids, cooling tower water, and recirculating systems. (2) Resistance to biological degradation is one of the properties that makes tolytriazole desirable as a corrosion inhibitor. Sodium di-(2-ethylhexyl) sulfosuccinate is a surfactant which is added to improve wetting properties.

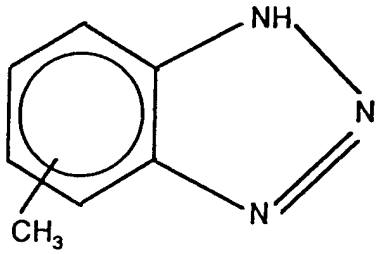


Figure 1. Structure of Tolytriazole

c. Commercial Deicers

Commercial Type I (unthickened) aircraft deicers contain ethylene glycol or propylene glycol for freezing point depression, a pH buffer, corrosion inhibitors, a wetting agent (surfactant), and a flame retardant. Diethylene glycol may be present as a minor constituent of the glycol portion. The flame retardant is tolytriazole. The corrosion inhibitor and surfactant are usually proprietary. Commercial Type II (non-Newtonian) deicers also contain a polymeric thickening agent. Commercial Type I and II designations do not correspond to military Type I and II designations which were explained above.

The Air Force has approved the use of propylene glycol based aircraft deicers meeting the commercial specifications. (3) The commercial deicers are in use at some Air Force Bases.

3. Effects on the Environment

a. Groundwater Contamination

Groundwater contamination is a possibility in permeable soils. Glycol moves through soil at very nearly the same rate as water. (1,4) Soil will not be frozen during the early and late portions of the deicing season. Water has been found to penetrate frozen soils through worm holes, vugs and fractures. (5) Ethylene/propylene glycol concentrations of up to 420 mg/L were found in groundwater at Ontario International Airport. (1) Peak levels occurred after spring runoff and declined to undetectable levels by fall.

b. Ethylene Glycol Toxicity

Concern over the toxicity of ethylene glycol and listing of ethylene glycol as a Hazardous Air Pollutant under the Clean Air Act, has caused the Air Force to phase out ethylene glycol aircraft deicers and replace them with propylene glycol deicers.

c. Environmental Impacts

Environmental impacts of glycol aircraft deicers include depletion of dissolved oxygen caused by the high biological oxygen demand (BOD) of the glycol component and contribution to the BOD_5, COD and aquatic toxicity of runoff. Microbial growth associated with biodegradation of the deicers may contribute to total organic carbon. The phosphate buffer contributes to phosphorous loadings, but in an amount less than that required for good microbial growth with propylene glycol as the carbon and energy source. Air pollution has not been a concern in deicing operations. Abiotic degradation of glycols is insignificant in comparison to biological degradation. The 5 day BOD (BOD_5) of propylene glycol is about 1 g/g. (1) Biodegradation of deicers also has the potential to produce objectionable odors due to the release of aldehydes. (1)

Several fish kills have been associated with deicer runoff including one at Pittsburgh IAP (host for 911TAG). Ethylene glycol in groundwater at Griffis AFB resulted in $8.2 million in Installation Restoration Program costs. (6) Plans for possible runoff collection and treatment facilities are included in Stormwater Management Plans, e.g., facilities for collection and diversion of Offutt AFB runoff to a wastewater treatment plant.

d. Conceptual Model for Distribution and Biological Degradation

A simplified conceptual model for the distribution and biological degradation of propylene glycol deicer in surface waters is shown in figure 2. (7) Deicer composition, deicer usage, weather, and hydrologic factors determine distribution and initial concentrations in surface waters. Collection systems, such as deicing pads, may reduce the amount of deicer

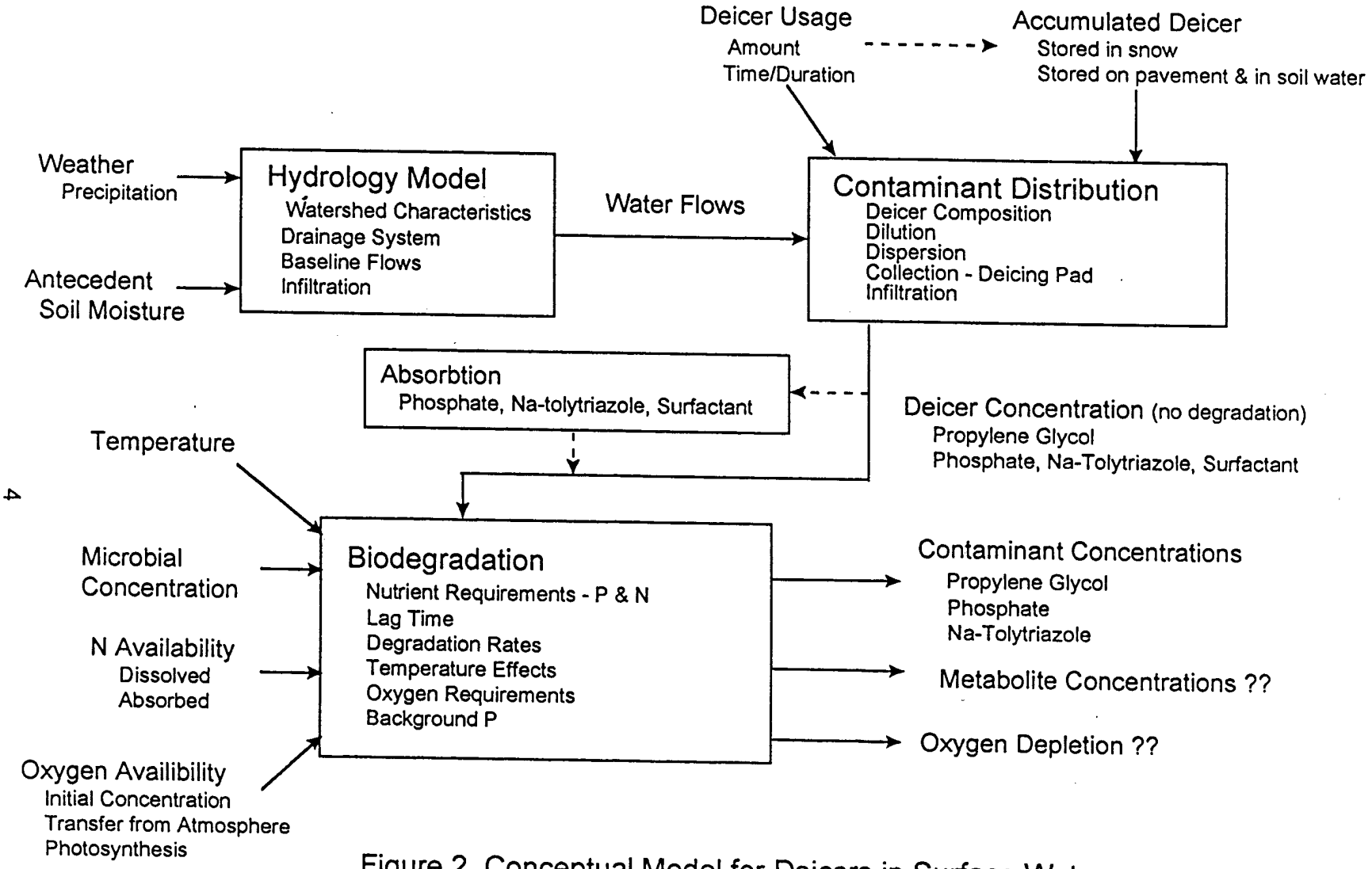


Figure 2. Conceptual Model for Deicers in Surface Waters

reaching receiving waters. Concentrations of additives may potentially be reduced by adsorption to soils and sediment. Propylene glycol will be biologically degraded in receiving waters. Microbial population and concentration, temperature, nutrient availability, and oxygen availability affect biodegradation rates. If oxygen usage exceeds reoxygenation, dissolved oxygen might be depleted.

e. Aquatic Toxicity

Information filed with the EPA under the Toxic Substances Control Act (TSCA) indicates that tolytriazole degrades very slowly and has an octanol-water partition coefficient of 72. (2,8) At the concentrations tested, tolytriazole was not toxic to microorganisms and did not inhibit degradation of other compounds. However, maximum tolytriazole concentrations expected in deicer runoff, based on deicer composition and glycol measurements, are greater than the tested concentrations. Partitioning of tolytriazole to soil, as seems likely based on the high octanol-water partition coefficient, could result in higher concentrations in the soil compartment. Aquatic toxicity for sodium tolytriazole is shown in Table 2.

Table 2. Aquatic Toxicity of Tolytriazole

Product / Composition	Toxicity Test	Toxicity
Cobratec® TT-100	Bluegill Sunfish - 96 hr Tlm	31 mg/L
Tolytriazole - 99% minimum	Minnow - 96 hr Tlm	25.5 mg/L
	Trout - 96 hr LC_{50}	21.4 mg/L
Cobratec® TT-50S	Bluegill Sunfish - 96 hr LC_{50}	191.2 mg/L
50% Sodium salt of	Rainbow Trout - 96 hr LC_{50}	23.7 mg/L
tolytriazole in water	Daphnia Magna - 14 day LC_{50}	13.2 mg/L
	Daphnia Magna - 21 day LC_{50}	5.8 mg/L

LC_{50} - concentration lethal to 50% of test organisms
Tlm - older equivalent to LC_{50}

Pillard (9) demonstrated that commercial deicers are more acutely toxic to aquatic organisms than their pure ethylene and propylene glycol counterparts. Organisms tested were *Pimephales promelas* and *Ceriodaphnia dubia*. Forty eight hour LC_{50}'s (concentration lethal to 50% of test organisms) for pure ethylene and propylene glycol were 34,400 and 18,340 mg/L for the more sensitive *C. dubia*. Corresponding LC_{50}s for ethylene and propylene glycol formulated deicers were 8,540 and 790 mg/L, respectively. Thus, most of the toxicity of the deicers tested was due to additives.

4. Environmental Regulations

Deicer runoff is covered by the EPA Stormwater Regulations (40 CFR 122.26), and a NPDES permit is required. Analysis of samples collected during storm events for oil and grease, pH, BOD_5, COD, TSS, total phosphorous, total Kjeldahl nitrogen, and nitrate plus nitrite nitrogen was required as part of permit applications. The regulations do not set specific discharge limits. A Stormwater Management Plan detailing potential methods for reducing pollution in stormwater runoff, evaluation of the methods, and plans for implementation are required.

Aircraft deicing will be exempt from a transportation equipment cleaning regulation to be promulgated by EPA under a proposal consent decree arising from litigation brought by the National Resources Defense Council. (10) EPA noted that stormwater permits cover deicing, and the permits require implementation of measures to reduce pollutants in stormwater runoff, which may solve the problem. EPA further commented that they will monitor the situation and add deicing to the transportation equipment cleaning regulation if the stormwater permit system doesn't solve the problem.

Deicer runoff may also be subject to local environmental regulations.

5. Biodegradation of Ethylene and Propylene Glycol

A number of studies have investigated biodegradation of glycols with more attention given to ethylene glycol than to propylene glycol. The initial rate of oxygen demand for propylene glycol is greater than for ethylene glycol, but the achievement of ultimate oxygen demand is less complete after 20 days. (1) Three studies were conducted using deicer formulations. Other studies did not include deicer additives.

Sabeh and Narasiah (11) investigated biodegradation of a commercial deicer in sequential reactors. Glycol composition of the deicer was 49% ethylene glycol and 5% diethylene glycol with the remainder being water and additives. Initial glycol concentrations ranged from 400 to 2800 mg/L. First order kinetics were found with k at 22°C decreasing from 1.6 to 0.07 d^{-1} as the substrate (as COD) to microorganism (as volatile suspended solids) ratio increased from 0.7 to 19.5. The rate constant dropped from 1.03 d^{-1} at 22°C to 0.29 d^{-1} at 10°C and 0.05 d^{-1} at 4°C. Jank, et al. (12) studied activated sludge treatment of two commercial deicers based on a mixture of ethylene glycol and propylene glycol at temperatures ranging from 2°C to 13.5°C. Deicing fluid was successfully treated in the system. Bioassay tests showed that toxicity of the effluent was due to toxicity of the sewage component. Increased nitrogen consumption was noted at lower temperatures.

Klecka, et al. (13) reported on the degradation of five commercial deicers in soil samples (sandy-loam) collected adjacent to the runway at the Tri-City Airport in Saginaw, Michigan. Diluted deicer was added to soil at 1 mL/20 g. A lag time was not observed. Average biodegradation rates at 25°C were 66.6 mg/kg-day for ethylene glycol and 83.5 mg/kg-day for propylene glycol. Average rates at 8°C were 19.7 mg/kg-day for ethylene glycol and 22.7 mg/kg-day for propylene glycol. Degradation was found to be zero order at concentrations above 100 mg/L.

Flatham, et al. (14,15) conducted a bench scale feasibility study for the cleanup of groundwater following an ethylene glycol coolant spill at the Naval Air Engineering Center in Lakehurst, NJ. The first order rate constants for ethylene glycol biodegradation were 0.8 d^{-1} with a lag time of about 4 days for a well mixed aerated sample and 0.5 d^{-1} in a static flask test. The initial ethylene glycol concentration was 1440 mg/L, and supplemental nitrogen and phosphorous were provided. Ethylene glycol was not toxic or inhibitory to the bacteria.

McGahey and Bouwer (16) found first order rate constants at 25 °C for 100-1,000 mg/L ethylene glycol to be 0.77 - 1.44 d^{-1} with a 2-3 day lag time for wastewater inoculum, 0.95 - 2.90 d^{-1} with a 0-3 day lag time for soil inoculum, and 0.76 d^{-1} with a lag time of <3

days for ground water inoculum. Omission of the nutrient supplement in one test using soil inoculum reduced the rate constant from 2.9 d^{-1} to 2.0 d^{-1}. Poor degradation at 10,000 mg/L was attributed to probable oxygen depletion.

Means and Anderson (17) measured degradation of ethylene glycol by biological oxygen demand, shake flask, CO_2 evolution, Gledhill (combined shake flask and CO_2 evolution) and activated sludge tests. Initial concentrations ranged from 1 to 210 mg/L depending on the test. Ethylene glycol degraded to 10% of the initial concentration in times ranging from 1 d for the activated sludge test to 10 d for the CO_2 evolution test.

Evans and David (18) simulated biodegradation of ethylene glycol at initial concentrations of 2 and 10 mg/L in water from four rivers at temperatures of 20, 8 and 4°C. Complete degradation occurred within 3 days at 20°C and within 14 days at 8°C. Degradation at 4°C was slower and was incomplete after 14 days for three of the four river water samples. The effect of sediment on degradation rates was tested by adding bottom sediment to water from two of the rivers. Bottom sediment increased degradation rates.

6. Reactions and Nutrient Requirements for Biological Degradation

a. Half Reactions

Half reactions for microbial growth are shown in equations 1, 2, and 3. (19) Examination of half reactions for cell synthesis shows that bicarbonate is consumed when ammonia is the nitrogen source, and that carbon dioxide is consumed when nitrate is the nitrogen source. Combining half reactions for carbohydrate and ethanol gives the half reaction for heterotrophic degradation of propylene glycol. Carbon dioxide, but not bicarbonate, is the product of the half reaction. Under equilibrium conditions, concentrations of bicarbonate and carbon dioxide are linked through the carbonate buffering system.

Equation (1) Organic Electron Donor

$$C_3H_8O_2 \text{ (Propylene Glycol)} + 4\,H_2O \longrightarrow 3\,CO_2 + 16\,H^+ + 16\,e^-$$

Equation (2) Cell Synthesis with Ammonia as Nitrogen Source

$$0.8\,C_5H_7O_2N + 7.2\,H_2O \longrightarrow 3.2\,CO_2 + 0.8\,HCO_3^- + 0.8\,NH_4^+ + 16\,H^+ + 16\,e^-$$

Equation (3) Oxygen as Electron Acceptor

$$8\,H_2O \longrightarrow 4\,O_2 + 16\,H^+ + 16\,e^-$$

b. Phosphorous and Nitrogen Requirements

Half reactions were combined using the method of Grady and Lim to give overall reaction as a function of cell yield. The overall reaction was then combined with nitrogen and phosphorous requirements for wastewater treatment plants (17) and with cell compositions (20) to obtain the estimated stoichiometric requirements shown in figure 3. Phosphorous in Mil-A-8243D Aircraft Deicer is shown for reference. The level of phosphorous in Mil-A-8243D Aircraft Deicer makes a significant contribution to phosphorous requirements, but it meets stoichiometric phosphorous requirements only at low biomass yields.

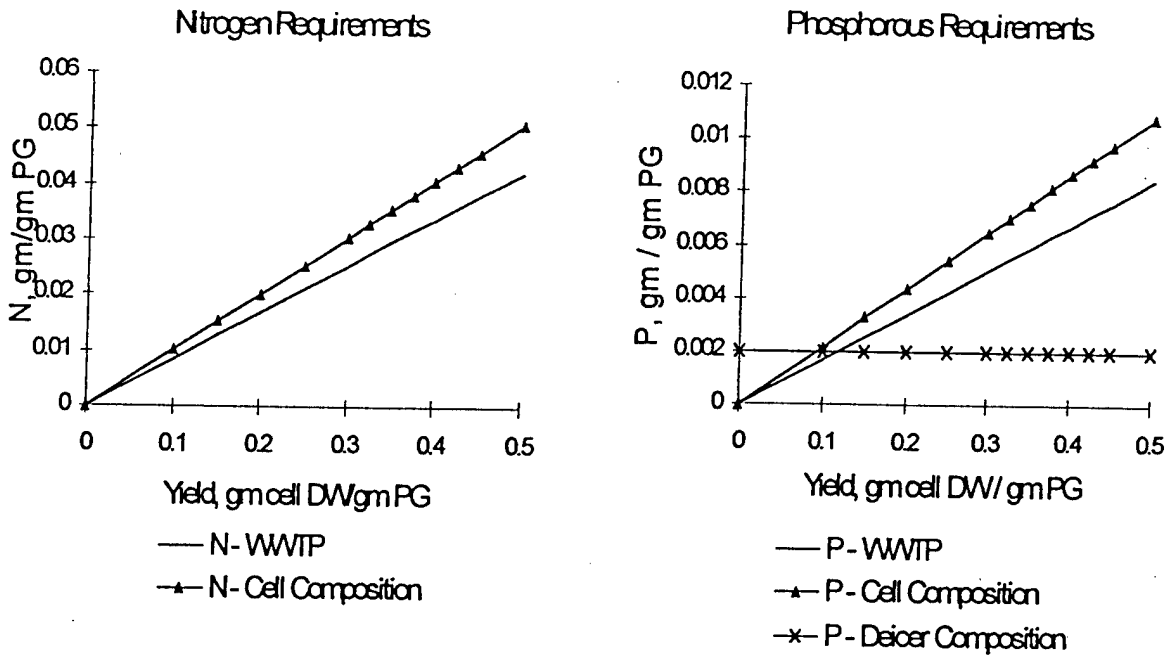
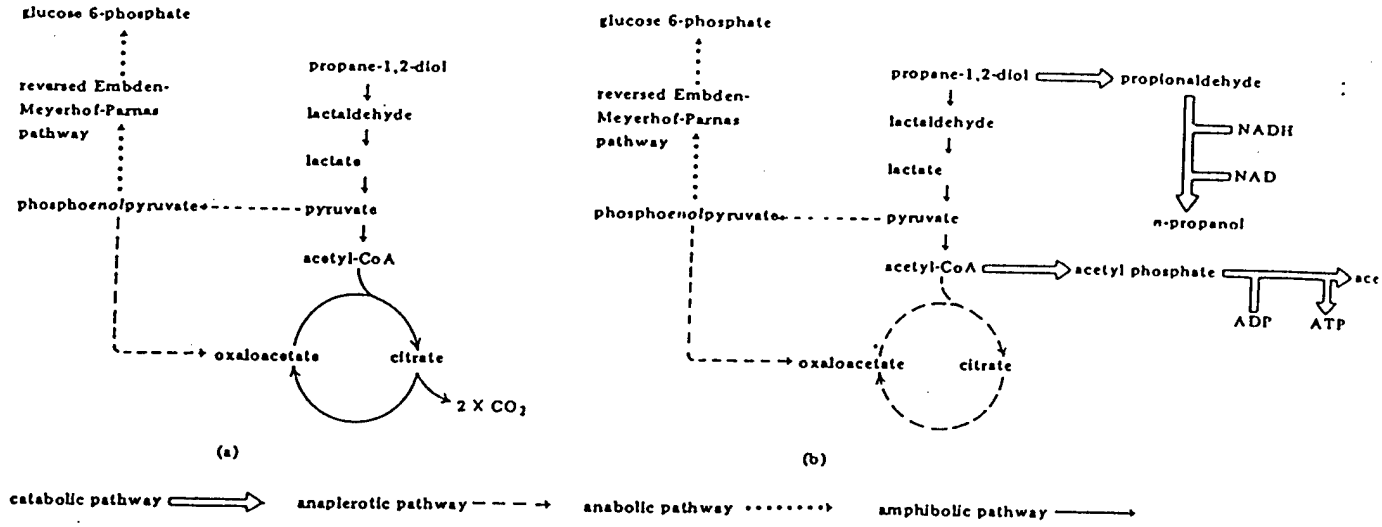


Figure 3. Nitrogen and Phosphorous Requirements Estimated from Half Reactions Combined with Wastewater Treatment Plant (WWTP) Nutrient Requirements and Elemental Cell Composition

7. Metabolic Pathways for Glycol Degradation

Various bacteria grown in pure culture have been found to metabolize ethylene and propylene glycol via the glyoxylate and tricarboxylic acid cycles. Glycol also may be metabolized to the corresponding aldehyde. The aldehyde may then be metabolized to CO_2 or, under microaerophilic conditions, reduced to the corresponding alcohol.

The aerobic metabolism of ethylene glycol and propylene glycol by *Flavobacterium* sp: NCIB 11171 has been investigated. (21,22,23) Pathways for propylene glycol are shown in figure 4. Under strongly aerobic conditions, *Flavobacterium* sp. NCIB 11171 metabolized propylene glycol to lactaldehyde and then pyruvate. Pyruvate was then oxidized to CO_2 via the tricarboxylic acid cycle. Under microaerophilic conditions, some propylene glycol was metabolized to propionaldehyde and subsequently reduced to n-propanol. N-propanol accumulated to a maximum of 36 mg/L after 36 hours of growth at a pO_2 of 30%. Growth was good at pO_2 greater than 60% and poor at pO_2 less than 40%. Lactate and lactaldehyde and/or 1-hydroxy, 2-propanone (acetol) were found in suspensions of sonically disrupted cells.



SCHEME I. Pathways of (a) aerobic and (b) microaerophilic metabolism of propane-1,2-diol by *Flavobacterium* sp NCIB 11171.

Figure 4. Pathways of metabolism of propylene glycol by *Flavobacterium* NCIB 11171, from Willets, 1979 (22)

Mycobacterium E44 metabolized ethylene glycol to acetaldehyde and then acetyl-CoA; the glyoxylate pathway was not utilized. (24) Acetylaldehyde accumulated up to stoichiometric amounts in washed cell suspensions. Propylene glycol was a poor substrate for the diol hydratase enzyme. Propylene glycol was a good substrate for the corresponding enzyme from *Aerobacter aerogenes.*

Metabolic pathways for aerobic degradation of ethylene glycol and polyethylene glycol by salt-requiring bacterium T-52 (25,26), an isolate (possibly an *Acinetobacter*) from sewage (27), and a soil bacterium (28) have been studied. Although degradation via the glyoxylate and TCA cycles was not proven, the studies did suggest and support degradation via those pathways. The soil bacterium also degraded propylene glycol. Pearce and Heydman (29) found three isolates, two from river water and one from soil, capable of degrading ethylene glycol but not propylene glycol. The isolates were assigned to the genus *Aeromonas.* Growth occurred on glycolate but not on acetylaldehyde, glycoaldehyde or glyoxal, suggesting metabolism via the glyoxylate pathway. A strain of *Pseudomonas aeruginosa* isolated from soil degraded ethylene glycol. (30)

Investigation of the microorganisms and metabolic pathways for glycol degradation by mixed cultures was not found in this review. Degradation of glycols by a mixed culture of bacteria, none of which is capable of metabolizing the glycols by themselves, should be considered a possibility.

Numerous species of *Acetobacter* and *Gluconobacter* have been demonstrated to oxidize ethylene glycol to glycolic acid. (31) Although optimum pH ranges for these bacteria are 5.4-6.3 and 5.5-6.0, respectively, bacteria of these genera are known to exist in canal water. Degradation of ethylene glycol by a mixed culture of *Acetobacter* or *Gluconobacter*

and bacteria capable of metabolizing glycolate (salt of glycolic acid) is a reasonable possibility.

Metabolic pathways for ethylene glycol have received much more attention than those for propylene glycol. This is partly because metabolism of ethylene glycol has been investigated as part of studies of polyethylene glycol degradation. Bacteria capable of metabolizing ethylene glycol may or may not be able to metabolize propylene glycol. If they are capable of metabolizing propylene glycol, different pathways may be used.

Propylene glycol also can be metabolized anaerobically. Gaston and Stadtman (32) investigated anaerobic degradation of propylene glycol by *Clostridium glycolicum*, a species isolated from mud from a stagnant pond. Anaerobic degradation resulted in equal concentrations of n-propanol and propionate.

SECTION II

METHODOLOGY

A. Analytical Methodology

1. Propylene Glycol and Metabolite Analysis

Concentrations of propylene glycol and metabolites other than organic acids were measured on a Hewlett Packard 5890 Series II gas chromatograph with a flame ionization detector. A 15 m X 0.53 mm Supelco Nukol Fused Silica Capillary Column was used with helium carrier gas. Injector and detector temperatures were 210°C and 260°C, respectively. The column temperature profile varied depending on which, if any, metabolites were being analyzed. For analysis of propylene glycol only, carrier gas flow rate was 14 mL/min with 140°C column temperature (Westover experiments) or 8 mL/min with 130°C column temperature (Buckley experiments). For analysis of propylene glycol and 1-hydroxy, 2-propanone the helium flow rate was 8 mL/min with a temperature profile of: initial temperature 95°C for 1.4 minutes followed by a 12.5 C/minute ramp to 140°C followed by 4 minutes at 140°C. Propionaldehyde, n-propanol and other non-acidic anoxic/anaerobic degradation products were analyzed by lowering the initial temperature to 75°C. Analytical error for propylene glycol analysis was 5-10% depending primarily on propylene glycol concentration, the presence of other compounds in samples and the age/condition of the column.

When the Hewlett Packard gas chromatograph was down, propylene glycol concentrations were measured on a Shimadzu Mini-GC 2 gas chromatograph equipped with a flame ionization detector and a Shimadzu C-R3A integrator. Helium carrier gas flowed at 30 mL/min through a 0.9 m X 0.26 cm glass column packed with 80/100 HayeSep Q. Injector, column and detector temperatures were 215 °C, 190°C, and 215 °C, respectively.

Propanoic acid and other organic acids were analyzed by high pressure liquid chromatography (HPLC) with a 300 mm X 7.8 mm Biorad Aminex HPX-87H column. The HPLC apparatus consisted of a Waters 700 Satellite WISP autoinjector, a Waters 501 HPLC pump, and Waters 486 Tunable Absorbance Detector set at 210 nm. The apparatus was controlled by a Waters Systems Interface Module connected to a personal computer. The mobile phase was 0.006 M H_2SO_4.

2. Sodium Tolytriazole Analysis

For degradation experiments, sodium tolytriazole concentrations were measured by high pressure liquid chromatography (HPLC) using with a 250 mm X 4.6 mm Biorad C18 column. The HPLC apparatus consisted of a Waters 700 Satellite WISP autoinjector, a Waters 501 HPLC pump, and Waters 486 Tunable Absorbance Detector set at 254 nm. The HPLC apparatus was controlled by a Waters Systems Interface Module connected to a personal computer. The mobile phase was a 40:60 mixture methanol and 0.08 M acetate buffer with pH 6. Flow rate was 1.1 mL/min.

For the octanol-aqueous phase partitioning coefficient experiments, sodium tolytriazole concentrations were determined by measuring absorbance on a Bausch and

Lomb Spectronic 21 spectrophotometer with the wavelength set at 295 nm. Octanol, but not water, absorbs at 525 nm. Separation of the aqueous and octanol phases was verified by measuring absorbance of the aqueous phase at 520 nm.

3. Microbial Density and Growth

Microbial growth was monitored by measuring optical density at 535 nm using a Perkin-Elmer Coleman 124 spectrophotometer.

4. Dissolved Oxygen

Chemitrics K-7510 Dissolved Oxygen colorimetric ampoules or a Hach DO-175 Dissolved Oxygen meter were used for measuring dissolved oxygen concentrations.

5. Ammonia and Nitrate

Ammonia and nitrate were measured colorimetrically using Hach NI-8 and Hach NI-11 test kits, respectively.

6. pH

A Corning 320 pH meter was used for pH measurements.

7. Soil Moisture

Soil moisture was determined by weighing samples before and after drying a 10-15 g soil sample to constant weight at 104°C.

8. Preparation of Deicer Formulation

Deicer was prepared from lab chemicals according to the component concentrations shown in Table 1. The deicer and propylene glycol stock solutions were formulated dilute to alleviate difficulties associated with high viscosity and so that measurable volumes could be added to water samples. Concentration of deicer and propylene glycol stock solutions ranged from 25,000 to 250,000 mg/L as PG depending on the desired concentration in the flasks. The pH was measured and checked against the allowable pH range for deicers. Chemicals used for formulating deicer were 1,2 propanediol (propylene glycol), dipotassium hydrogen phosphate, dibasic anhydrous (K_2HPO_4) and sodium di-(2-ethylhexyl) sulfosuccinate from Fisher Acros. Sodium tolytriazole was aqueous sodium tolytriazole, 50% by weight, from PMC Specialties Group used without further purification.

B. Experimental Methodology

Degradation of contaminants, including propylene glycol, in the environment is commonly simulated in the laboratory in shake flasks, static flasks and soil microcosms. To simulate aqueous degradation, water collected from the field is amended with the contaminant of interest and incubated in a shake flask or static flask. The aqueous environment may be manipulated, for example by adding nutrients or changing the pH, in order to determine which factors are limiting degradation rates.

Degradation in soil is simulated in soil microcosms prepared by adding the contaminant of interest to soil in culture tubes. The tubes are incubated. At appropriate intervals, the remaining contaminant is extracted from the soil. The extract is then analyzed for the contaminant.

1. Degradation in Westover AFRB Water

Two series of shake flask experiments were conducted to determine propylene glycol degradation rates and the effects of deicer additives, nutrients and pH on propylene glycol degradation rates. Water for the experiments was provided by Westover AFRB. The water was collected from the ditch that drains the portion the base that includes the area where aircraft deicing is conducted. Samples were shipped via overnight delivery and used immediately after receipt. Density of propylene glycol degrading microorganisms was 6,700 CFU per mL as determined by plate counts using 2,500 mg/L propylene glycol in agar supplemented with nitrogen, phosphorous and sulfur sources. Plates were incubated at room temperature (24-27°C) for four days. Optical density at 535 nm was 0.05, and the pH was 7.9.

The first set of experiments was run in 250 mL flasks containing 90 mL each of water provided by Westover AFRB. Autoclaved solutions of deicer or propylene glycol were added to the flasks resulting in the concentrations shown in Table 3. A phosphate buffer and nutrient solution containing ammonium nitrate and sodium sulfate were added to six of the flasks to test for nutrient limitations. Sterile deionized water was added to flasks not receiving the buffer and/or nutrient solutions to give equal total volume in all of the flasks. The total volume in each of flasks was 93 mL. The pH of all flasks except W6 and W9 was adjusted to pH 7.9 by adding, as necessary, dilute hydrochloric acid. Flask W6 was adjusted to pH 9.0. The flasks were incubated in a refrigerated incubator at 20°C and 150 rpm.

Autoclaved controls with 1,000 and 100 mg/L of propylene glycol were included in the test series. A "dirty" control, W11, was run to verify that pH and dissolved oxygen measurements did not contaminate flasks. W11 was checked for pH and dissolved oxygen on the same schedule as W4 and W5.

The second set of experiments tested the effect of deicer additives and phosphorous limitation on degradation rates. Inoculum and medium for the second set of experiments consisted of 10 mL decanted from a stock culture grown on propylene glycol and diluted with a total of 90 mL of sterile deionized water and stock solutions. Stock solutions of propylene glycol, deicer additives, phosphate buffer, and nutrients were added resulting in the phosphate and additive concentrations shown in Table 4. The ammonia concentration was 160 mg/L as N, and the sulfate concentration was 9 mg/L as S. The pH was adjusted to 7.9, and the 250 mL flasks were incubated at 20°C and 150 rpm.

Table 3. Concentrations for First Set of Westover Experiments

Flask	Description	Propylene Glycol, mg/L	Deicer as Propylene Glycol (PG), mg/L	Phosphate as P, mg/L	Ammonia as N, mg/L	Sulfate as S, mg/L	Initial pH
W1	PG with Buffer & Nutrient	5,000		620	160	9	7.9
W2	Deicer with Buffer & Nutrient		5,000	620	160	9	7.9
W3	PG Unbuffered	1,000		2			7.9
W4	PG with Buffer & Nutrient	1,000		620	160	9	7.9
W5	Deicer Unbuffered		1,000	2			7.9
W6	Deicer Unbuffered, High pH		1,000	2			9.0
W7	Deicer with Buffer & Nutrient		1,000	620	160	9	7.9
W8	PG with Buffer & Nutrient	100		620	160	9	7.9
W9	Deicer Unbuffered		100	2			8.1
W10	Deicer with Buffer & Nutrient		100	620	160	9	7.9
W11	Deicer Control (Dirty)		1,000	620	160	9	7.9
W12	Deicer Control		1,000	620	160	9	7.9
W13	Deicer Control		100	620	160	9	7.9

Table 4. Concentrations for Second Set of Westover Experiments

Flask	Description	Added Phosphate as P, mg/L	Additive
W-21	PG Control	620	None
W-22	Deicer	620	Na-TTA / 6.3 mg/L Na di-(2-ethylhexyl) sulfosuccinate / 5.7 mg/L
W-23	Phosphate Limited	2	Phosphate per deicer composition
W-24	PG with Na-tolytriazole	620	Na-TTA / 6.3 mg/L
W-25	PG with surfactant	620	Na di-(2-ethylhexyl) sulfosuccinate / 5.7 mg/L

Concentration in all flasks - 1000 mg/L propylene glycol, 160 mg/L ammonia as N, and 9 mg/L sulfate as S.
Basal salts: MgCl 16 mg/L, KCl 16 mg/L, Na_2SO_4 50 mg/L, $CaCO_3$ 16 mg/L, $FeSO_4$ 22 mg/L.

2. Degradation in Westover AFRB Soil

A soil sample was taken from the bottom of the ditch that drains areas where deicer is used. A background sample was taken from the area above the ditch, opposite the pavement. Both samples were taken from a depth of 18 inches. The samples were stored at 4°C until used in experiments. Soil characteristics are shown in Table 5.

Table 5. Characteristics of Westover AFRB Soil

Ditch Sample	Sand	90%
	Silt	6%
	Clay	4%
	Texture	Sand
	Total Nitrogen	0.055%
	Nitrate N	1.9 mg/kg
	Total Organic Carbon (TOC)	0.30%
	Soil Moisture	7.3%
Background Sample	Sand	45%
	Silt	21%
	Clay	34%
	Texture	Clay Loam / Sandy Clay Loam
	Soil Moisture	4.6%

All analyses except soil moisture performed by CSU Soil, Water and Plant Testing Laboratory.

Soil was prepared by sifting through a No. 10 soil sieve to remove roots and rocks and to breakup any clumps. Microcosms were prepared by placing 20 grams each of moist soil in 50 mL culture tubes. Control microcosms were autoclaved three times at three day intervals for thirty minutes each time. Soil moisture lost during autoclaving was replaced by addition of sterile deionized water. One mL of 3,500 mg/L deicer as PG was added to each tube, and deicer mixed by gently rolling and shaking the tube. Soil was then compacted by shaking.

Tubes were sealed and incubated at 20°C. Deicer was extracted with 10 mL of deionized water at various times up to 24 days. The extract was decanted and centrifuged to remove any remaining soil particles, then analyzed for propylene glycol.

3. Degradation in Buckley ANGB Water, Williams Pond

a. Buckley ANGB Water Samples

Deicer runoff from the two deicing areas on Buckley ANGB can drain to two creeks and to the on-base Williams Pond. The two creeks were dry when water for the experiments was collected, so the water was taken from Williams Pond. Williams Pond does not have a surface outlet and is known for algae growth. Because the pond surface was completely frozen over, water samples were taken through a hole chopped in the ice. Approximately 15 aquatic insects, commonly referred to as water boatmen, from the genus *Corixidae*, were observed in the 6 L of water collected. The water also contained small copepods. Water was stored at 4°C until used for experiments.

The water had a pH of 9.8, and the absorbance at 535 nm was 0.21. Duplicate plate counts were run using agar with 2,500 mg/L propylene glycol plus nitrogen, phosphorous and basal salts. The plates were incubated at room temperature (22°C) for 8 days. The measured concentrations of propylene glycol degrading microorganisms were 27,000 and 36,000 CFU/mL. The water had a noticeable green tinge from the algae. Results of analysis by the CSU Soil, Water and Plant Testing Laboratory are shown in Table 6. The sample was filtered before analysis.

Table 6. Buckley ANGB Water Analysis

Total Kjeldahl Nitrogen (TKN)	2.43 mg/L
Nitrate	10.2 mg/L
Total Phosphorous	0.21 mg/L
CO_3	121.6 mg/L
HCO_3	400.3 mg/L
Alkalinity as $CaCO_3$	531 mg/L

b. Shake Flask Experiments

Shake flask experiments were conducted to determine propylene glycol degradation rates and the effects of temperature and nutrients on degradation rates. One static flask, B-35, was run to check degradation and metabolite formation at lower dissolved oxygen concentrations such as might be encountered in ponds or deeper water. Nitrogen and phosphorous additions were less than estimated requirements for good growth based on a yield of 0.3 - 0.4 gm cells DW per gm propylene glycol.

Stock solutions of deicer, propylene glycol, potassium phosphate and ammonium chloride were added to 250 mL flasks containing 100 mL of Buckley water resulting in the concentrations shown in Table 7.

c. Effects of pH

Effects of pH were checked by incubating flasks with starting pH values of 7.5 and 9.0 at room temperature. Each flask contained a 100 mL aliquot of sterile deionized water containing 1000 mg/L deicer as PG, 310 mg/L phosphate buffer as P, and 1 mg/L ammonium chloride as N, basal salts, and inoculum consisting of washed cells from a stock culture.

d. Nitrogen Sources

A set of static tests was run to determine whether the microorganisms could use urea as the nitrogen source. Four 40 mL aliquots of water amended with 1000 mg/L deicer as PG and 3 mg/L P (including P in deicer) were incubated at room temperature in 50 mL culture tubes. Three of the tubes received 10 mg/L N by adding ammonium chloride, ammonium nitrate and urea, respectively. The fourth flask received 25 mg/L of potassium chloride as Cl resulting in the same chloride concentration as for ammonium chloride addition. After five days, samples were taken for ammonia and propylene glycol analysis.

Table 7. Concentrations for Buckley Experiments

Flask	Propylene Glycol, mg/L	Deicer as PG mg/L	Phosphate as P, mg/L	Ammonia as N, mg/L	Notes
Incubator Temperature 20°C					
B-31		3500	7		
B-32		1000	2		
B-33		1000	2		
B-35		1000	2	20*	Static Flask
B-36		1000	2	20	
B-38	1000			5 & 1*	
B-39	1000		2		Na-TTA 60 mg/L
B-40		350	0.7		
B-41		350	0.7		
B-42		350	0.7	7	
B-43		350	1.4		
B-44	350				
B-45		100	0.2		
B-47		1000			Control
B-48		350			Control
B-50		1000	4	20	Plus Basal Salts
Incubator Temperature 10°C					
B-51		350	0.7		
B-52		350	0.7	7	
B-53		100	0.2		
B-54		35	0.07		
B-55		10	0.01		

* B35 added on day 5; B-38 added on days 8 and 12.

e. Anaerobic / Anoxic Degradation Tests

Experiments under anaerobic / anoxic conditions were conducted in 50 mL culture tubes to determine metabolites from anaerobic / anoxic degradation and to test possible sources of reported odors. (1,33) Propylene glycol, ammonium chloride and phosphate were added to the Buckley water resulting in concentrations of 1,500 mg/L propylene glycol, 20 mg/L ammonia as N and 1.5 mg/L phosphate as P, respectively. Oxygen was removed by bubbling helium through the water for 15 minutes. Two of the culture tubes received 25 mL each of the amended water. These tubes were then shaken by hand to provide slight reaeration resulting in dissolved oxygen of 1.5 mg/L. The mouths of these tubes were covered with foam plugs. A third culture tube was filled to the top with 50 mL of amended water and had a dissolved oxygen level of less than 1 mg/L. This culture tube was closed with a foil lined screw top cap. Samples were taken at 3, 5, and 11 days. An additional sample was taken from the third tube at 13 days.

Upon completion of the above anaerobic / anoxic experiments, the potential for sulfur reduction was checked using the third culture tube. Propylene glycol, nutrients, sodium sulfate, lysine, and cystiene (additions were not measured) were added, and the tube resealed to prevent oxygen transfer from the atmosphere.

f. Propylene Glycol and Propylene Glycol Metabolite Toxicity Test

Propylene glycol, potassium phosphate monobasic and ammonium chloride were added to water from Buckley ANGB resulting in concentrations of 3,500 mg/L PG, 0.5 mg/L ammonia as N and 16 mg/L phosphate as P. Aliquots of 130 mL each were incubated at 20°C for 19 days and then 3 days at room temperature (24°C). Additional nitrogen was fed in the form of urea instead of ammonia to minimize the possibility of ammonia toxicity to test organisms. On days 3 and 5, 0.6 mg/L-medium of urea as N was added. Nitrogen feeding was suspended until it was determined that precipitates were interfering with the colorimetric ammonia nitrogen test causing false (high) results. Nitrogen feeding was resumed on day 12. Nitrogen was fed in the form of urea: days 12-13 and 17-19, 0.6 mg/L-medium as N; and days 20-21, 1.2 mg/L-medium as N. A second set of flasks was prepared with starting concentrations of 10,000 mg/L PG, 0.8 mg/L ammonium as N, and 48 mg/L P.

Two raw water and four samples from propylene glycol degradation were sent to ENSR, Ft. Collins, CO for aquatic toxicity testing. One of the raw water and three of the propylene glycol samples were centrifuged to remove cells and other solids. Static 48-hour acute toxicity tests were run with *Ceriodaphnia dubia* as the test species.

Individual deicer components were tested at concentrations equivalent to 3,500 mg/L deicer as PG. Samples containing 35,000 mg/L propylene glycol, 398 mg/L (71 mg/L as P) dibasic potassium phosphate, 200 mg/L sodium di-(2-ethylhexyl) sulfosuccinate, and 220 mg/L sodium tolytriazole in deionized water were submitted to ENSR. ENSR diluted the samples to 10% of original concentration with moderately hard water and tested for aquatic toxicity.

4. Degradation in Buckley ANGB Soil

Soil samples were collected from a depth of 18 inches for use in determining deicer degradation rates in soil. A sample was submitted to the CSU Soil, Water and Plant testing Laboratory for determination of texture. The soil was a clay loam / sandy clay loam containing 45% sand, 21% silt and 34% clay.

Soil microcosms were prepared by adding 1 mL of deicer solution to 50 mL culture tubes containing 20 gm of soil. Due to the clay and silt content, the soil could not be packed to original condition, and deicer could not be reliably extracted. Since potential for infiltration in this soil is low, soil degradation rates should be of limited interest. Additional effort was not spent attempting to overcome the packing and extraction difficulties.

5. Sodium Tolytriazole Partition Coefficient

The effect of propylene glycol on the octanol-water partition coefficient was checked by determining the partition coefficient between octanol and water containing 0, 550 and 30,000 mg/L of propylene glycol.

Octanol and sodium tolytriazole solutions were placed in 50 mL centrifuge tubes and agitated on a shaker table for 12 hours at 20°C. The sodium tolytriazole solution was buffered with 6 mM of potassium phosphate dibasic, and the pH adjusted to 7.9 by drop wise addition of hydrochloric acid. Propylene glycol solutions, 10,000 mg/L and 100%, were

then added resulting in the initial tolytriazole and propylene glycol concentrations shown in Table 8. Octanol and aqueous-phase volumes in mL were 15, 15; 20,12; 20, 8; and 20,4.

Table 8. Initial AqueousTolytriazole Concentrations

Initial Na tolytriazole, mg/L	Propylene glycol, mg/L
1000	None
950	550
970	30,000

The octanol phase was removed with a Pasteur pipette. The aqueous phase was centrifuged at 15,000 g for 15 minutes, and any additional separated octanol was removed. Octanol separation and removal from the aqueous phase was verified by turbidity measurements. Sodium tolytriazole concentrations were then measured by UV spectrophotometry.

Sodium tolytriazole was extracted from 5 mL of octanol taken from the 1:1 volume ratio experiment with no propylene glycol in the aqueous phase. Sodium tolytriazole was extracted with 10 mL of 6 mM phosphate buffer. Agitation, separation and analysis were the same as above.

SECTION III

RESULTS AND DISCUSSION

A. Propylene Glycol and Deicer Degradation in Westover AFRB Water

1. First Set of Experiments

There was no measurable loss of propylene glycol from the controls.

Degradation of propylene glycol from the first set of experiments, W1 - W10, using Westover water is shown in figure 5. A lag time of about 2 days is indicated for all starting concentrations whether or not additional nutrients were provided. Concentration changes in the first 2 days were within the range of analytical error. For 5,000 mg/L, the end of the lag time is concealed by the high propylene glycol concentration.

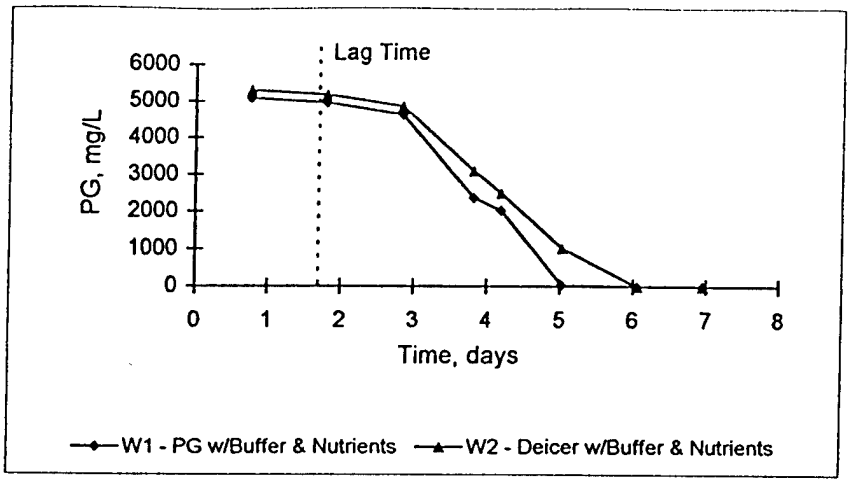
Data depicted in figures 5(a), 5(b) and 5(e) for flasks with added nutrients were not sufficient to allow modeling. However, it is readily apparent that neither exponential nor straight line curves fit the data. The general shape of the curves is consistent with Monod kinetics in batch reactors with a high initial substrate concentration and low initial microbial concentration.

Without added nutrients, propylene glycol degradation was slower than when nitrogen, phosphorous and sulfur were added, figures 5(c), 5(d) and 5(e). At 100 mg/L deicer as PG, nutrients were sufficient to allow complete disappearance of propylene glycol within 4 days. At 1000 mg/L without additional nutrients, figure 5(c), degradation was faster for the deicer than for propylene glycol. This result suggests that phosphorous was the limiting nutrient, and phosphorous from the phosphate buffer in the deicer was sufficient to promote growth and degradation for between 4 and 5 days The rate of propylene glycol disappearance from flasks receiving the deicer decreased after 4 days. Nutrient depletion, probably of either phosphorous or nitrogen is indicated. If it is assumed that phosphorous from the deicer is depleted at 5 days and no phosphorous was present in raw field water, a phosphorous requirement of 0.008 mg-P/mg propylene glycol can be estimated.

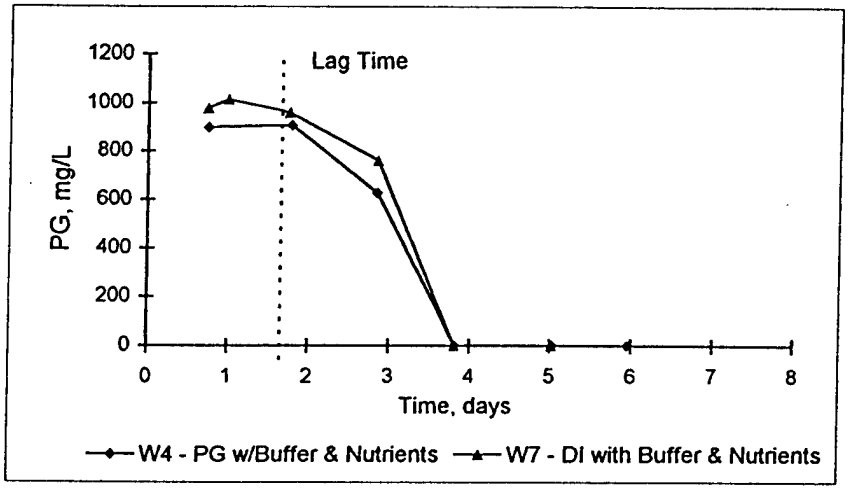
Under nutrient limited conditions, the data are best modeled as three phases. The first phase is the lag phase during which the microbial concentration is increasing to levels that will consume substrate at significant rates. During the second phase, sufficient nutrients are present for growth and relatively rapid substrate consumption. The final phase is the nutrient limited phase characterized by reduced microbial concentration and slower degradation rate. Propylene glycol disappearance rates during the second and third phases calculated by linear regression are given in Table 9.

Table 9. Propylene Glycol Disappearance Rates - Westover AFRB Water

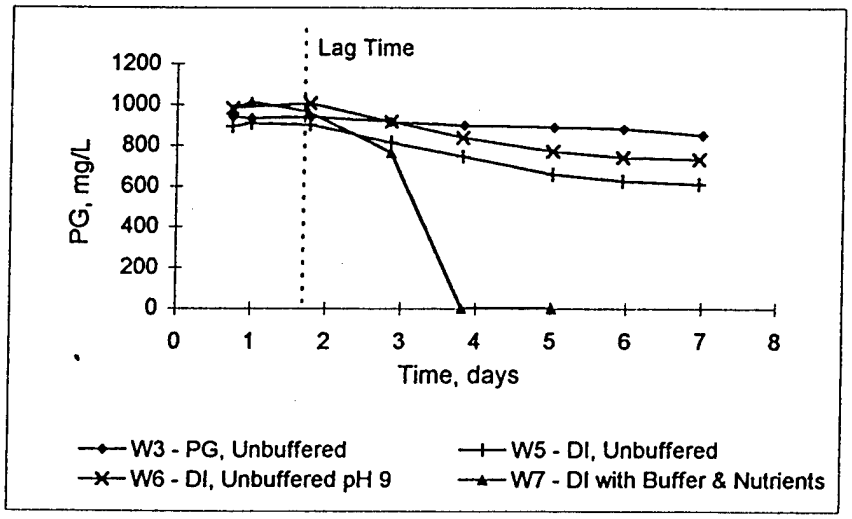
	Phase 2	R^2	Phase 3	R^2
W3, 1000 mg/L PG	Not Applicable		15.5 mg/L/day	0.95
W5, 1000 mg/L Deicer	76 mg/L/day	0.999	25 mg/L/day	0.96
W6, 1000 mg/L Deicer	83 mg/L/day	0.999	20 mg/L/day	0.94
W10, 100 mg/L Deicer	>50 mg/L/day		Not Applicable	



(a)

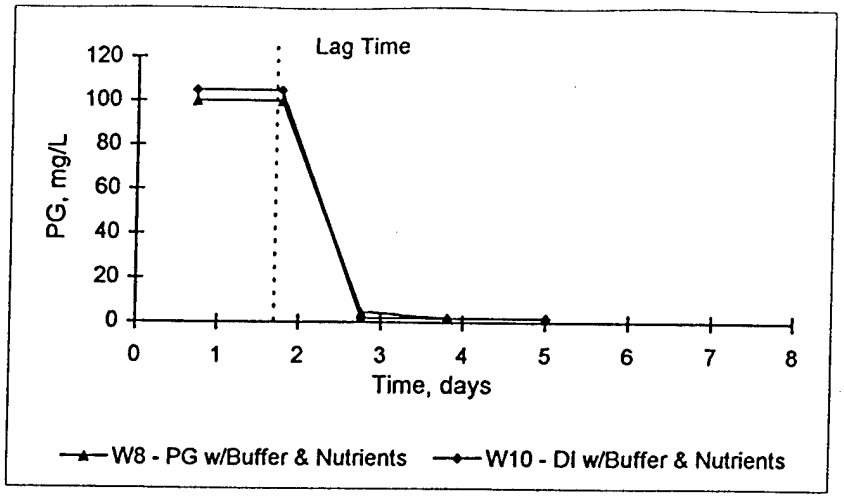


(b)

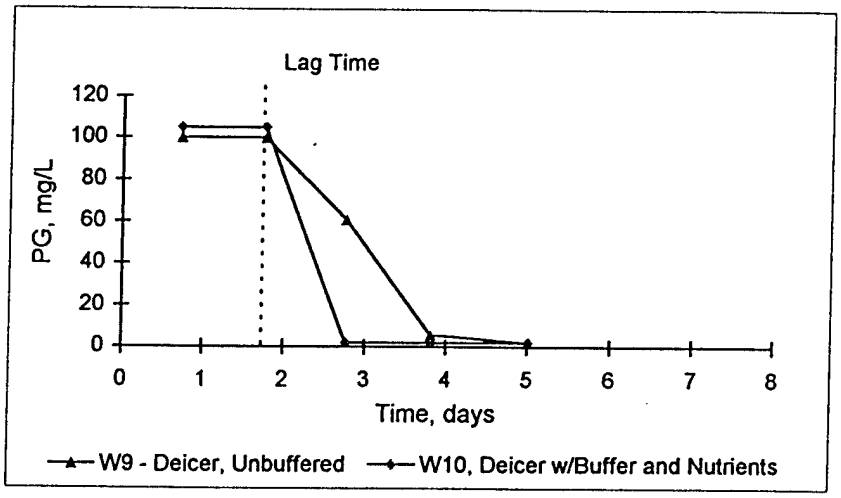


(c)

W1, W2, W4, W7, W8, W10: Phosphate Buffer - 620 mg/L as P and Nutients - Ammonia, 160 mg/L as N, Sulfate 9 mg/L as S



(d)



(e)

W1, W2, W4, W7, W8, W10: Phosphate Buffer - 620 mg/L as P and Nutients - Ammonia, 160 mg/L as N, Sulfate 9 mg/L as S

Figure 5. (Cont) Propylene Glycol Degradation Westover AFRB, W1-W10

Visual observations of growth generally fell into three stages with times depending on growth within each flask. A period of increasing turbidity was followed by formation of a granular floc and then a heavy floc. Finally, the water became clear, and large clumps of debris appeared in the bottom of the flasks at about the time of propylene glycol substrate or nutrient depletion. Due to floc formation and settling in samples, absorbance measurements were considered poor indicators of microbial concentration. Absorbance increases were generally consistent with propylene glycol disappearance up to the time when settling and floc formation made measurements impossible.

The pH at day 6 for the 5000 and 1000 mg/L flasks with added buffer and nutrients (W1,W2, W4 and W6) averaged 7.5. The pH in flasks that did not receive additional nutrients (W3, W5 and W6) was 8.2. The difference is consistent with greater disappearance of propylene glycol. Likely mechanisms are consumption of alkalinity and/or production of acidic degradation products, either of which would increase the equilibrium hydrogen ion concentration and thus decrease the pH.

Dissolved oxygen was tested using colorimetric ampoules. The ampoules indicated high or low oxygen levels but were not quantitative. Low levels of dissolved oxygen corresponded with rapid degradation of propylene glycol. Oxygen may have been limiting during periods of rapid growth and substrate degradation.

Upon completion of the experiments, the dry cell mass was determined for flasks W4 and W7. Yields of 0.45 and 0.5 gram cells DW per gram propylene glycol substrate were calculated. The presence of ammonia in flasks receiving additional nutrients confirmed that sufficient nitrogen had been added to meet requirements. The phosphorous requirement obtained from figure 3 for cell yields of 0.45-0.5 gram cells per gram PG is 0.007-0.011 gram-P/gram PG, which agrees with the 0.008 gram-P/gram PG estimated above.

2. Metabolites

Selected samples were analyzed for metabolites. The only metabolite detected by gas chromatography was 1-hydroxy, 2-propanone. Measurements are given in Table 10. Analysis by High Pressure Chromatography (HPLC) was negative for propanoic acid. Hydroxy propanone disappeared at the same time as or before propylene glycol was depleted. A split 1-hydroxy, 2-propanone peak was observed. The split peak was investigated as part of experiments with Buckley ANGB water, and the problem is discussed in paragraph III.B.2 below.

Table 10. Westover AFRB, Concentration of 1-Hydroxy, 2-Propanone Metabolite

Flask	Time, days	Concentration, mg/L
W2	3	27
W2	4.5	ND
W2	6	ND
W4	3	21
W4	4	ND
W4	5	ND
W5	3	3
W5	7	9

3. Second Set of Westover Experiments

Data from the second set of Westover experiments are shown in figure 6. As indicated by the measurable concentration of propylene glycol after 1.5 days, propylene glycol degradation was slightly slower when the surfactant, sodium di-(2-ethylhexyl) sulfosuccinate, was present. The phosphorous limited flask showed much slower disappearance of propylene glycol. The pH of this flask was adjusted to 7.6 at 2.5 and 4 days when the pH measured 3.8 and 6.8, respectively.

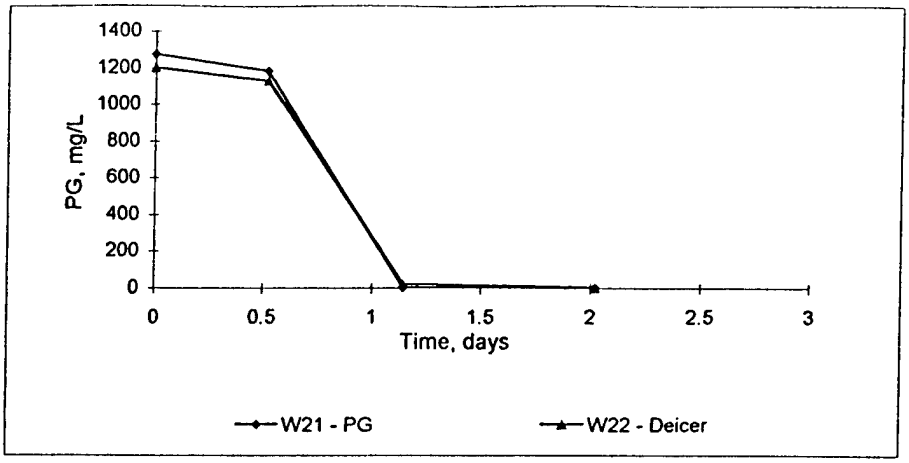
Slower degradation in flasks containing the surfactant was probably not due to inhibition. A greater tendency to form floc was observed in these flasks and a heavy ring formed on the glass at the liquid surface. Regardless of the cause, the slightly slower degradation is not likely to be important to degradation in the environment.

B. Deicer Degradation in Westover AFRB Soil

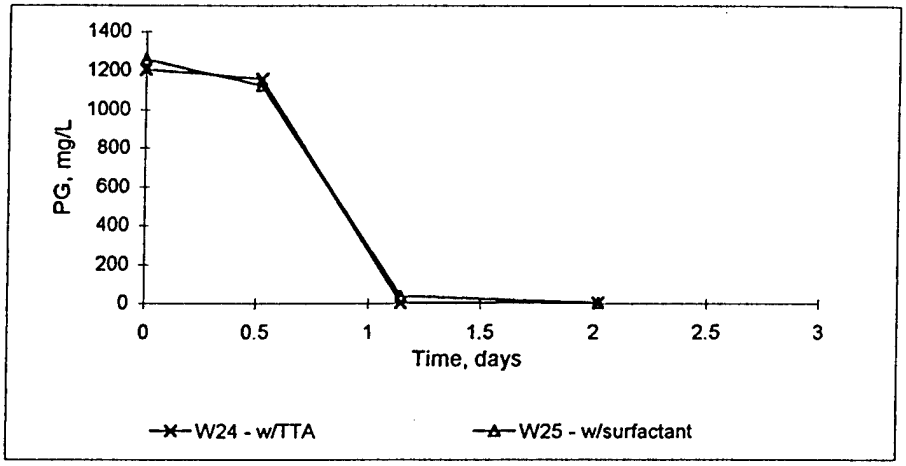
Results of degradation experiments in soil from Westover AFRB are presented in figure 7. A lag time of about 4 days is apparent in the graph. Degradation rates following the lag time are given in Table 11. Loss of propylene glycol from the control was negligible. The degradation rate in the soil from the bottom of the ditch was seven times faster than in the background sample. The reason for the higher degradation rate was not determined. Degradation rates for this study were an order of magnitude lower than rates found by Klecka (13) in soil collected next to the runway at the Tri-City Airport in Saginaw.

Table 11. Degradation Rates in Westover AFRB Soil

Sample Series	Degradation Rate, mg-PG / kg-soil	R^2
Bottom of Ditch - Control	0.1	0.04
Bottom of Ditch	3.8	0.61
Background Soil	0.5	0.25



(a)



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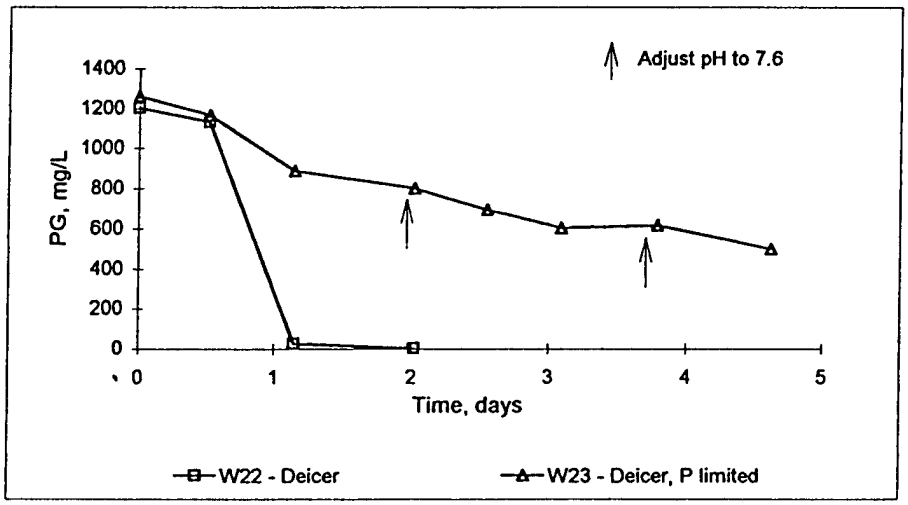


(c)

All Flasks - Ammonia, 160 mg/L as, Sulfate, 9 mg/L as S
W21, W22, W24, W25 - Phosphate Buffer, 620 mg/L as P
W23 - Phosphate 2 mg/L as P per Deicer Composition
W24 - Na-Tolytriazole 6.3 mg/L per Deicer Composition
W25 - Na di-(2-Ethylhexyl) Sulfosuccinate, 5.7 mg/L per Deicer Composition

Figure 6. Propylene Glycol Degradation Westover AFRB, W21-W25

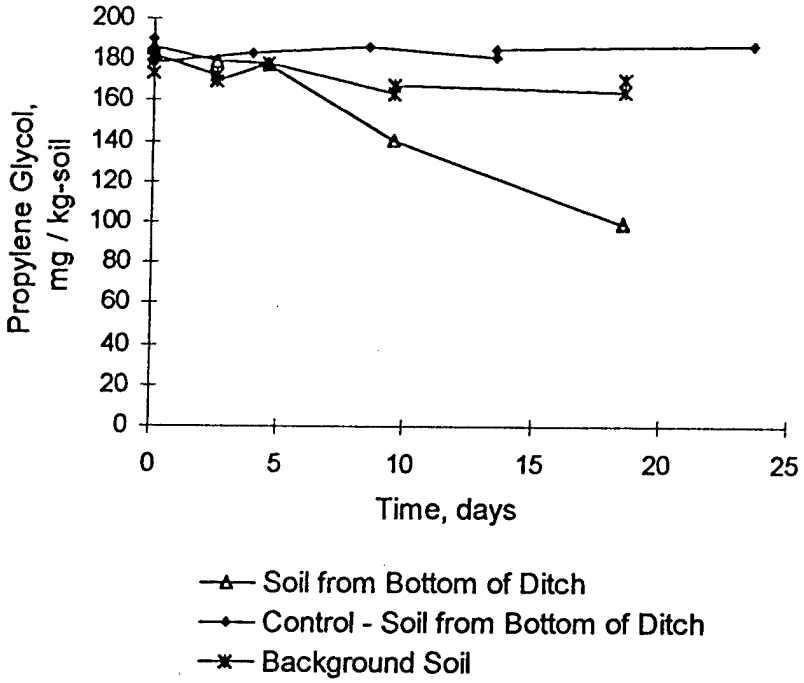


Figure 7. Degradation of Deicer in Westover AFRB Soil

C. Propylene Glycol and Deicer Degradation in Buckley ANGB Water

1. Degradation Rates at 20°C

There was no loss of propylene glycol from the control B48. There was a loss of 100 mg/L propylene glycol from control flask B47. 1-hydroxy, 2-propanone was detected in B47 but was not quantified. Disappearance of propylene glycol from B47 appears to be an anomaly.

Propylene glycol concentrations for the 20°C Buckley experiments are shown in figure 8. Interferences with the ammonia nitrogen test by a precipitate, even when Rochelle's reagent was used, prevented measurement of ammonia nitrogen. Varying concentrations of algae would have made optical density measurements impossible to interpret, so measurements were not made.

A lag time of 2-4 days is apparent for all of the flasks. Degradation without added nutrients was slow. Degradation rates in flasks determined from linear regression of concentrations following the lag time are shown in Table 12. Differences in the degradation rates were not statistically significant. For B32 and B33, a slight downward trend is evident. A good fit could not be obtained because concentration changes were the same order of magnitude as analytical error. Phosphorous was not limiting for the Buckley water.

Table 12. Degradation Rates for 20°C Flasks without Added Nutrients

Flask	Solution	Degradation Rate	R^2
B40	Deicer - 350 mg/L	12 mg/L/day	0.998
B41	Deicer - 350 mg/L	12 mg/L/day	0.997
B43	Deicer - 350 mg/L w/ supplemental P	11 mg/L/day	0.933
B44	Propylene Glycol - 350 mg/L	10 mg/L/day	0.978
B45	Deicer - 100 mg/L	10 mg/L/day	0.951

Maximum degradation rates for B36 and B42, which received additional phosphorous and nitrogen, occurred just after the lag time. For B36, the maximum degradation rate obtained by linear regression was 325 mg/L/day using 2 data points and 225 mg/L/day using 3 data points. For B42, the maximum rate obtained by linear regression was130 mg/L/day using 2 data points and 100 mg/L/day using 3 data points.

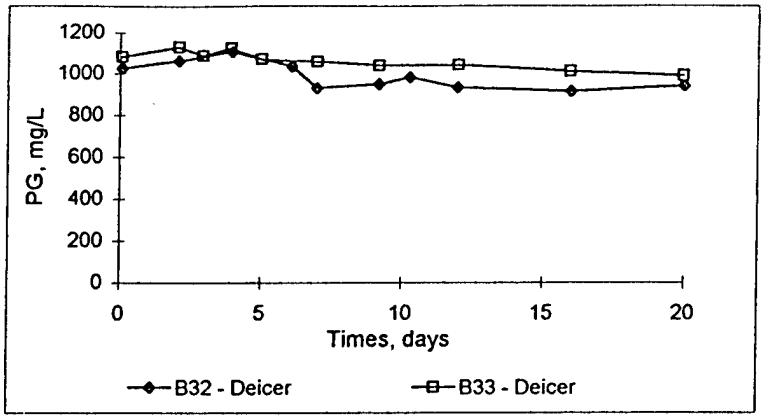
Nitrogen addition resulted in markedly higher degradation rates in B35, B36, B42, and B50. Nitrogen limitation is indicated. The 2.4 mg/L of TKN should have supported good growth and rapid degradation until 100-200 mg/L PG had been consumed. Since good growth and degradation did not occur without supplemental nitrogen, it is concluded that nitrogen was either not in a readily available form or the concentration was kinetically limiting. More rapid degradation in B50 than B36 might be attributable to the extra phosphorous. A total of 6 mg/L nitrogen was added to B38 -- 5 mg/L after 5 days and 1 mg/L after 12 days -- and degradation became apparent after a lag time. B38 received propylene glycol instead of deicer, and phosphorous likely became a limitation after nitrogen addition. The break in the degradation curve for B38 at 17 days was likely caused by nitrogen depletion. B35 was a static flask experiment, and lower degradation can be attributed to poor mixing and low oxygen concentrations.

A rough estimate of nitrogen requirements is obtained by dividing the propylene glycol degraded into the sum of measured TKN and added nitrogen but ignoring any nitrogen obtained from solids (primarily decaying algae). The resulting estimated range for the nitrogen requirement is 0.016 to 0.022 gram N per gram propylene glycol.

2. Temperature Effects

Propylene glycol disappearance from shake flasks incubated at 10°C is shown in figure 9. The experiments were terminated early when cooling was lost due to a freon leak. Flasks B51 and B52, which had starting concentrations of 350 mg/L, exhibited a lag time of between 2 and 5 days, while flasks with lower starting concentrations did not exhibit a lag time. Early degradation at the higher concentration may be masked by the lower absolute accuracy of the concentration measurements at higher concentrations.

Degradation rates in flasks determined from linear regression of concentrations following the lag time are shown in Table 13.



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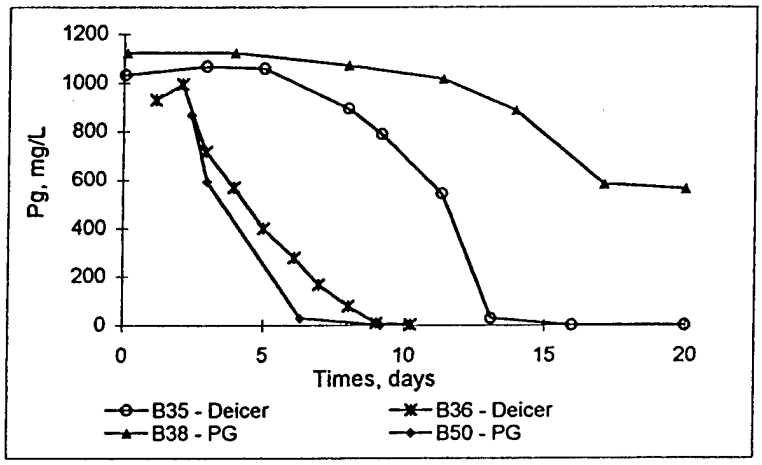

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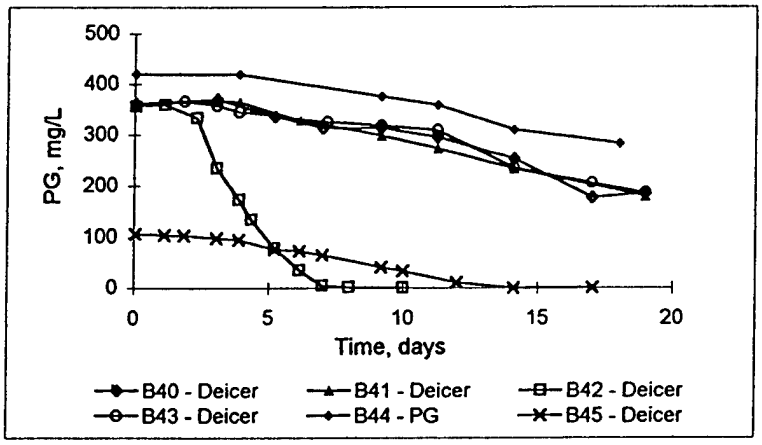
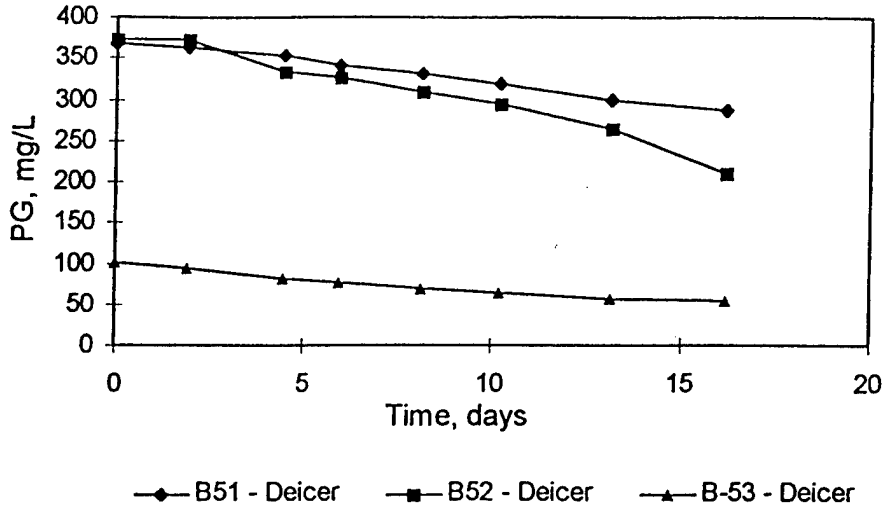


(c)

B35 (Static Flask) - 20 mg/L ammonia as N (added day 5),
B36 - 20 mg/L ammonia as N, B38 - 5 mg/L ammonia as N (added day 8) and
1 mg/L ammonia as N (added day 12), B42 - 7 mg/L ammonia as N,
B43 - supplemental phosphorous 0.7 mg/L phosphate as P,
B50 - 20 mg/L ammonia as N and supplemental phosphorous 4 mg/L as P

Figure 8. Propylene Glycol Degradation at 20°C, Buckley ANGB



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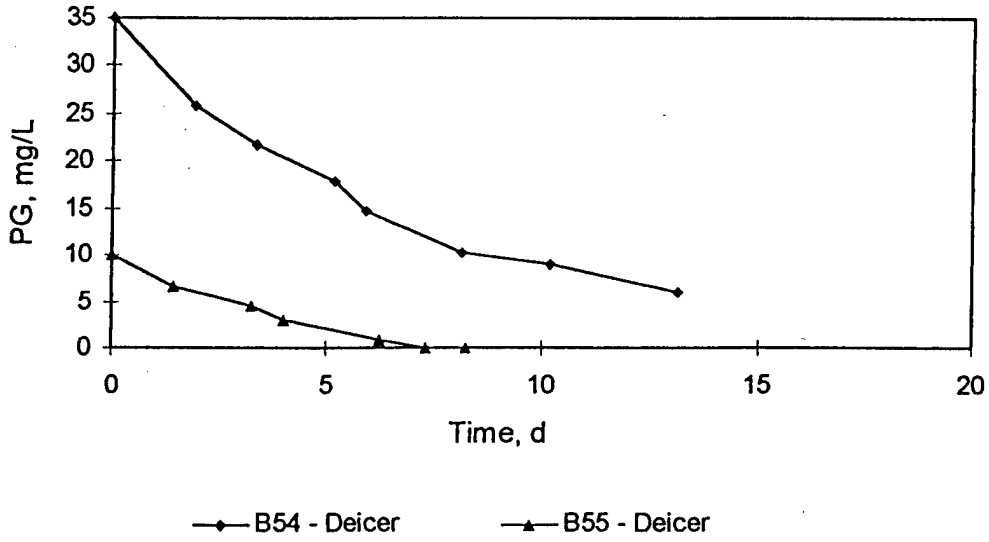


(b)

B52 - 7 mg/L ammonia as N

Figure 9. Propylene Glycol Degradation at 10°C, Buckley ANGB

Table 13. Degradation Rates for 10°C Flasks without Added Nutrients

Flask	Solution	Degradation Rate	R^2
B51	Deicer - 350 mg/L	5.2 mg/L/day	0.98
B53	Deicer - 100 mg/L	2.8 mg/L/day	0.98
B54	Deicer - 35 mg/L	2.1 mg/L/day	0.92
B55	Deicer - 10 mg/L	1.3 mg/L/day	0.97

Equation 4 is often used to describe the effects of temperature on rate constants.

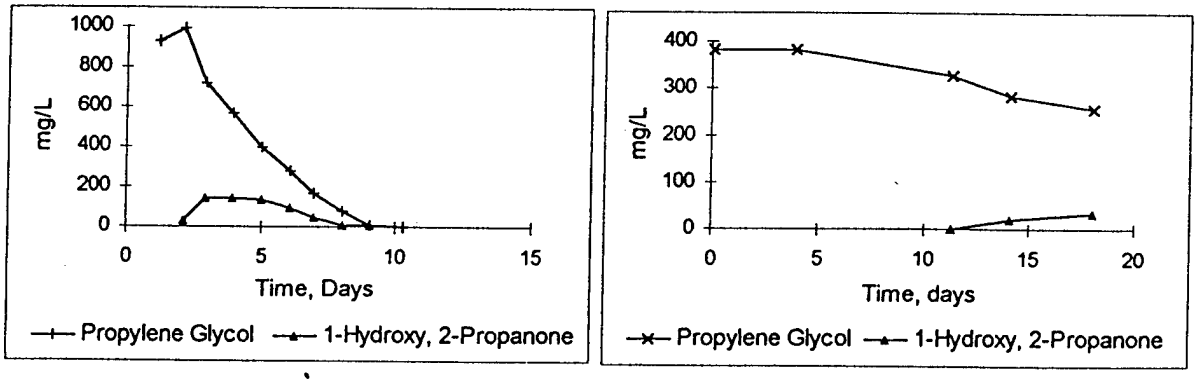
$$\text{Equation 4:} \quad k_1 = k_2 \times \theta^{(T1-T2)}$$

where k_1 and k_2 are rate coefficients at temperatures T1 and T2 in ^{o}C, and θ is a thermal coefficient. θ can be estimated from the12 mg/L/day and 5.2 mg/L/day propylene glycol degradation rates measured at 20°C and 10°C with starting concentrations of 350 mg/L as PG. Calculation yields a value for θ of 1.09. However, the reliability of the value is poor because of uncertainty in the degradation rates and because the characteristics of the raw Buckley water and the microbial population may have changed between the start of the 10°C and 20°C experiments. The 10°C temperature is at the lower end of the temperature range for mesophiles, and it is possible that temperature effects are not described by equation 4. The value is considerably higher than the 1.00 to 1.04 range typical of activated sludge systems. (34) Calculating θ from average degradation rates found by Klecka in soil (13) yields a value of 1.08.

Continuous stirred tank reactor (CSTR) experiments may be better suited for determining the temperature dependency of degradation rates. CSTR experiments could provide for collection of multiple data points at each temperature and reduce the uncertainty in the determination of degradation rates.

3. Aerobic Metabolites

1-Hydroxy, 2-propanone was identified as the major intermediate metabolite in aerobic propylene glycol degradation. Concentrations in flasks B36 and B44 shown figure 10 were typical of degradation in the Buckley water. Higher metabolite concentrations were associated with more rapid propylene glycol degradation.



(a) Flask B36 (b) Flask B44

Figure 10. Aerobic Metabolites

Pyruvate at less than 2 mg/L was identified by liquid chromatography as a metabolite in B36 on day 6. There were several other peaks that could not be identified. One of the unidentified peaks was probably lactate or succinate. Several unidentified peaks, some of which corresponded to peaks in B36, were observed in samples from the pH effects test and the toxicity tests. The significance of the unidentified peaks is uncertain since the HPLC/UV response of compounds is highly variable.

The hydroxy propanone peak for several of the flasks was split on GC/FID analysis using both the capillary and packed columns. The first part of the split peak should have eluted on GC/MS just after the water peak. GC/MS, which was run using a different column, showed only one peak, which was identified as hydroxy propanone. This issue was not satisfactorily resolved. The discussion of Willets (22) suggests lactaldehyde may have been responsible for the split peak.

4. Anoxic / Anaerobic Degradation Products

Maximum concentrations of major metabolites and byproducts measured in anoxic / anaerobic cultures are shown in Table 14. Dissolved oxygen levels at the end of the test were 3.4 mg/L for the "open" tubes and 1.3 mg/L for the sealed tube. Although fluid in the tubes was mixed prior to sampling either by gently inverting the tubes or by swirling, results indicated incomplete mixing. Sampling procedures for dissolved oxygen measurements likely added some oxygen.

The compounds were identified by gas chromatography/mass spectrometry (GC/MS) and verified by matching retention times with standards. The 1-hydroxy, 2-propanone peak was split in some of the samples as in the aerobic cultures.

Table 14. Anaerobic / Anoxic Degradation Products, Buckley ANGB Water

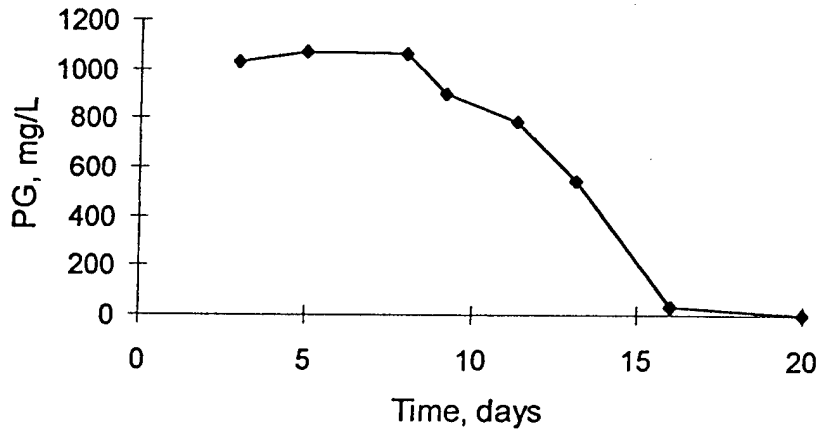
Metabolite / Byproduct	Maximum Concentration, mg/L	Sample
Anaerobic (Sealed) Tube		
propionaldehyde	260	Day 11
n-propanol	285	Day 11
unknown	110	Day 11
1-hydroxy, 2-propanone	60	Days 8 and 13
Anoxic ("Open") Tubes		
propionaldehyde	120	Day 5
n-propanol	110	Day 11
unknown	46	Day 5
1-hydroxy, 2-propanone	94	Day 5

A sample taken from the sealed tube on day 11 was analyzed by high pressure liquid chromatography for propanoic acid and other organic acids. Propanoic acid, lactic acid and acetic acid were present at concentrations of 480, 20 and 10 mg/L, respectively. Pyruvic acid and formic acid were present at concentrations less than 2 mg/L. Propanoic, acetic and formic acid peaks were also identified during GC/MS analysis.

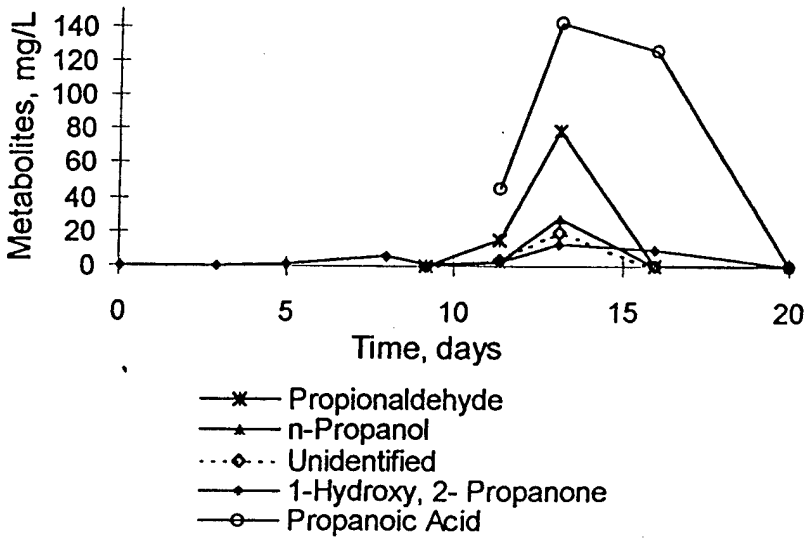
Several minor peaks were observed in chromatograms obtained with FID analysis. On GC/MS, the peaks were either not observed, were too small for identification or eluted with the water peak.

Concentrations of propylene glycol and four major metabolites for B35, a static flask experiment, are shown in figure 11. Significant concentrations of metabolites characteristic

of anoxic / anaerobic metabolism were measured on days 11 and 13. Concentrations for propionaldehyde, n-propanol, an unidentified compound, and propanoic acid are shown in figure 11(b). Several minor peaks were also apparent in gas chromatograms obtained on those days. Additional peaks also appeared in liquid chromatograms. However, their significance is uncertain since the HPLC/UV response of compounds is highly variable. Dissolved oxygen levels on days 5, 11, 16, and 20 were 1.0, 2.6, 1.9, and 3.4 mg/L. Floc formation became apparent at 9 days. Concentrations of all of these metabolites were at zero or trace levels by the 20th day except for lactic acid and the unidentified peaks in the liquid chromatograms. Acetic acid and lactic acid were found at concentrations less than 15 mg/L. Pyruvic and formic acid were found at levels below 1 mg/L. The final pH for this flask was 8.7.



(a)



(b)

Figure 11. Metabolite Formation - B35, Static Flask
2 mg/L Phosphate as P (Initial), 20 mg/L Ammonia as N (Added Day 5)

Environmental conditions in the flask allowing anaerobic degradation could have been present on either of two environmental scales. Oxygen deficient microenvironments in the floc and attached growth may have been the sites for anaerobic metabolism. Alternatively, anaerobic degradation may have occurred on a macroenvironmental scale due to insufficient oxygen to support aerobic metabolism.

The static flask and culture tube experiments demonstrated the potential for anaerobic degradation in this water when sufficient nutrients are available. Propionaldehyde, n-propanol and propanoic acid were identified as major metabolites. One major peak and several minor peaks were also apparent in the GC/FID analysis of samples from anaerobic / anoxic degradation.

5. Aquatic Toxicity

Results of 48 hr *Ceriodaphnia dubia* aquatic toxicity testing are shown in Table 15. Neither propylene glycol nor the metabolites were toxic. The 20% survival for centrifuged raw water was anomalous and is believed to be due to contamination from glassware. Degradation in flasks containing 10,000 mg/L was not measurable. 1-Hydroxy, 2-propanone was detected at low levels. The probable cause is substrate inhibition by propylene glycol. Water from these flasks was not submitted for toxicity testing.

Table 15. Aquatic Toxicity Test Results

Sample	Incubation Time	Propylene Glycol, mg/L	1-Hydroxy, 2-Propanone, mg/L	Average 48 hr Survival
Buckley Water	NA	NA	NA	100
Buckley Water *	NA	NA	NA	20
T51	0 days	3500	0	100
T52	19 days	2800	450	100
T53	22 days	2500	520	93.3
T54 (Not centrifuged)	22 days	2300	460	100

Survival rates for propylene glycol, dibasic potassium phosphate, sodium di-(2-ethylhexyl) sulfosuccinate, and sodium tolytriazole at concentrations equivalent to 3,500 mg/L deicer as PG were 100%, 100%, 0%, and 30%, respectively. Thus, the surfactant, sodium di-(2-ethylhexyl) sulfosuccinate, and the flame inhibitor, sodium tolytriazole, were more toxic than propylene glycol and metabolites of propylene glycol degradation.

6. Odor

The anoxic / anaerobic culture developed a slightly sweet odor described as fruity, similar to that in bread making and beer fermentation. By the end of the test, the odor had become strong enough to be considered noxious. A slight odor was noticed in the faster growing aerobic cultures, particularly in the static flask experiment.

Propionaldehyde is probably the major contributor to the noxious odor. Propanoic acid smells slightly sweet, similar to acetic acid but not nearly as strong. Acetol and n-propanol have little or no odor. The odor of propionaldehyde is described in the literature as

suffocating. (35) The propionaldehyde odor observed in this investigation while mixing standards at moderate concentrations (around 100 mg/L) was similar to the noxious odor observed in the anoxic / anaerobic culture experiments. At higher concentrations (above 500 mg/L) the suffocating smell was obvious. The slightly sweet component of the culture's odor was probably due to propanoic acid and possibly to acetic acid as well.

The culture tube with added sulfur containing compounds produced the typical hydrogen sulfide / mercaptan odor indicating sulfur reduction.

7. Sodium Tolytriazole Degradation

B39 was spiked with 60 mg/L of the Na tolytriazole flame retardant. Figure 12 shows the disappearance of both Na tolytriazole and propylene glycol. Disappearance of tolytriazole coincided with propylene glycol degradation and was greater than can be

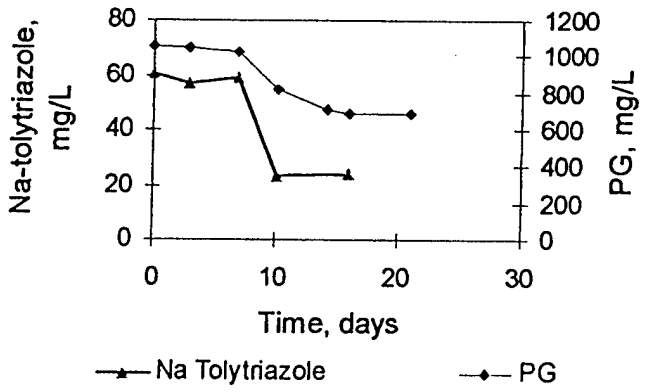


Figure 12. Na Tolytriazole Degradation

accounted for by partitioning to organic carbon. Products of Na tolytriazole degradation were not determined, and it is unknown whether all isomers were degraded. Nitrogen in the tolytriazole, as well as the added phosphorous, may have contributed to the increased degradation rates as compared to those in unspiked flasks without supplemental nutrients. Results of this test need to be confirmed by further experimentation.

D. Sodium Tolytriazole Partition Coefficient

Partitioning of sodium tolytriazole between the aqueous and octanol phases is described by the partition and material balance equations:

Equation (4) $C_{oct} = K_{o\text{-}aq} * C_{aq}$

Equation (5) $C_{aq\,o} * V_{aq} = C_{aq} * V_{aq} + C_{oct} * V_{oct}$

where C_{oct} is the concentration in octanol, C_{aq} is the concentration in the aqueous phase,

$K_{o\text{-}aq}$ is the octanol-aqueous phase partition coefficient, $C_{aq\,o}$ is the initial concentration in the aqueous phase, V_{aq} is the volume of the aqueous phase, and V_{oct} is the volume of the octanol phase.

Equations 4 and 5 above can be combined and rearranged to give the equation:

Equation (6) $C_{aq\,o} / C_{aq} = 1 + K_{o\text{-}aq} * (V_{oct} / V_{aq})$

$K_{o\text{-}aq}$ was determined by linear regression of C_{aq} data. The results are presented in Table 16.

Table 16. Sodium Tolytriazole Octanol-Water Coefficient ($K_{o\text{-}aq}$)

	$K_{o\text{-}aq}$	95% Confidence Interval
Na Tolytriazole in Water	57.7	51.3 - 64.0
Extraction from octanol	60	NA
Na Tolytriazole in 550 mg/L Propylene Glycol	53.2	42.1 - 64.3
Na Tolytriazole in 30,000 mg/L Propylene Glycol	51.6	45.7 - 57.5

The slight decrease in $K_{o\text{-}aq}$ observed at higher propylene glycol concentrations was statistically insignificant. A K_{ow} of 72.4 is reported in TSCA documentation. The solubility of sodium tolytriazole increases with pH, and the partition coefficients may have been affected by the higher pH used in this study. Within the context of uncertainties associated with any attempt to determine the distribution of sodium tolytriazole in the environment, the observed differences in values are small.

SECTION IV

CONCLUSIONS

A. Degradation Rates and Nutrient Limitation in Aqueous Phase

Propylene glycol degradation rates were limited by the availability of nitrogen and phosphorous in the water.

Propylene glycol degradation in water from Westover AFRB was limited by the availibility of phosphorous. Degradation of propylene glcyol in deicer was accelerated relative to pure propylene glycol by phosphorous from the phosphate buffer. Shake flasks with a 1,000 mg/L initial concentration of deicer as PG exhibited a lag time of approximately 2 days. The lag phase was followed by a phase of rapid growth and substrate consumption during which propylene glycol disappeared at rates of 76-83 mg/L/day. Propylene glycol disappearance during the final, nutrient limited phase, was 20-25 mg/L/day. When propylene glycol was added instead of deicer, the rapid growth and substrate consumption phase was absent. Following the lag phase, propylene glycol disappeared at a rate of 16 mg/L/day. Degradation in flasks receiving supplemental nitrogen and phosphorous was rapid, and propylene glycol was depleted within 6 days.

Water from Buckley ANGB was more limited in nitrogen than phosphorous, and propylene glycol degradation for both deicer and pure propylene glycol was slow. Flasks with initial concentrations of 350 mg/L of propylene glycol exhibited a 2-4 day lag time followed by degradation rates of 10-12 mg/L/day. Addition of supplemental nitrogen in the form of ammonia resulted in markedly higher degradation rates.

In phosphorous limited waters, phosphorous in the phosphate buffer may be sufficient to promote microbial growth and degradation of the propylene glycol component of deicers as was observered in water from Westover AFRB. However, the phosphorous may be insufficient to support complete degradation of propylene glycol depending on background phosphorous present and cell yields. Due to the nutrient effects of the phosphate buffer, environmental degradation rates from propylene glycol studies should be applied to deicer degradation cautiously, if at all.

B. Modeling of Propylene Glycol Degradation

Batch degradation of the propylene glycol component of deicer without nutrient supplementation can be empirically modeled in three phases. The first phase is the lag time. Propylene glycol degradation is minimal while the microbial density is increasing to levels where degradation is significant. During the second phase, sufficient nitrogen and phosphorous nutrients are available to support relatively rapid growth and propylene glycol consumption. During the third phase, nitrogen or phosphorous is depleted and degradation slows markedly. The second phase will be absent if nutrient availability is very low, and the third phase will be muted or absent if nutrient availability is high.

C. Additives

The surfactant and flame retardant did not have a significant effect on propylene glycol degradation rates. The effects of the phosphate buffer were discussed above. One of the shake flasks with Buckley ANGB water was spiked with 60 mg/L of the sodium tolytriazole flame retardant. Disappearance of tolytriazole coincided with propylene glycol degradation and was greater than can be accounted for by partitioning to organic carbon. The nutrient effects of nitrogen from the tolytriazole, as well as the added phosphorous, may have provided additional nutrients contributed to the increased propylene glcyol degradation rates. The observed degradation of tolytriazole is encouraging considering the slow degradation reported in TSCA documentation. (8) Results of this test need to be confirmed by further experimentation.

D. Metabolites and Intermediates

1-Hydroxy, 2-propanone was identified by gas chromatography as the major intermediate in aerobic degradation of propylene glycol. Maximum concentrations detected were 27 mg/L and 142 mg/L for the Westover AFRB and Buckley ANGB experiments, respectively. A sample from flask B36, a flask from Buckley ANGB experiments that received deicer and supplemental nitrogen, was analyzed by high pressure liquid chromatography (HPLC) with a UV detector. Pyruvate was detected at less than 2 mg/L. Another peak was probably lactate or succinate, and there were also several other peaks that could not be identified.

The 1-hydroxy, 2-propanone peak was split in gas chromatograms indicating that a second compound was probably present. The discussion of Willets (22) suggests lactaldehyde may have been responsible for the split peak. Hydroxy propanone was not persistent and disappeared before or within 1-2 days after depletion of propylene glycol.

Propionaldehyde, n-propanol, propanoic acid, and an unidentified compound were the major metabolites in anoxic/anaerobic degradation of propylene glycol in nutrient supplemented water from Buckley ANGB. Several minor peaks were also noted in gas chromatograms. Lactic acid, acetic acid, pyruvic acid, and formic acid were also detected. These metabolites were observed in sealed and open culture tubes and in a static flask experiment, B35. Dissolved oxygen levels in B35 ranged from 1.0 to 3.4 mg/L. Propylene glycol was consumed within 16 days. Concentrations of all measured metabolites were at zero or trace levels except lactic acid and the unidentified peaks in liquid chromatograms.

Anecdotal reports of objectionable odors are probably due to propionaldehyde. Another possibility is production of hydrogen sulfide and mercaptans.

Metabolites and intermediates observed were in agreement with previous pure culture studies except that a major metabolite corresponding to the unidentified compound in gas chromatograms was not reported in literature.

E. Temperature Effects

For the Buckley ANGB water, the degradation rate at 10°C was 43% of the rate at 20°C. The relative magnitude of degradation rates is considered unreliable due to uncertainties in

degradation rates and because the microbial population may have changed between the start of the 20°C experiments and the 10°C experiments. Continuous stirred tank reactor (CSTR) experiments may be better suited to determining the temperature dependency of degradation rates. CSTR experiments could allow for collection of multiple data points at each temperature and reduce the uncertainty in the determination of degradation rates.

F. Aquatic Toxicity

Aquatic toxicity tests showed that propylene glycol and metabolites of propylene glycol were not acutely toxic to *Ceriodaphnia dubia*. Toxicity tests were run on Buckley ANGB water with an initial propylene glycol concentration of 3500 mg/L and phosphate corresponding to phosphate in deicer at a concentration of 3500 mg/L as PG. Nitrogen was provided by feeding urea during incubation. Survival rates for water with the surfactant, sodium di-(2-ethylhexyl) sulfosuccinate, and the flame inhibitor, sodium tolytriazole, at concentrations equivalent to 3500 mg/L deicer as PG were 0% and 30%, respectively. Thus, the surfactant, sodium di-(2-ethylhexyl) sulfosuccinate, and the flame inhibitor, sodium tolytriazole, were more toxic than propylene glycol and metabolites of propylene glycol degradation.

G. Degradation in Soil

Propylene glycol degradation in soil from Westover AFRB was 3.8 mg-PG/kg-soil/day in a sample from the bottom of the ditch that drains areas where deicing is conducted and 0.5 mg-PG/kg-soil/day in a background soil sample following a 4 day lag time. Degradation rates found in this study were an order of magnitude lower than rates found by Klecka (13) in soil collected adjacent to the runway at the Tri-City Airport in Saginaw, Michigan. The reason for the comparatively low degradation rates was not determined.

H. Partitioning of Sodium Tolytriazole

Octanol-water partition coefficients measured in this study ranged from 52 to 60. The slight decrease in the octanol-water partition coefficient observed at higher propylene glycol concentrations was statistically insignificant. A K_{ow} of 72.4 is reported in TSCA documentation. The partition coefficients may have been affected by the higher pH used in this study. Within the context of uncertainties associated with any attempt to determine the distribution of sodium tolytriazole in the environment, the observed differences in values are small.

I. Applicability of Results

Microbial concentrations and populations and the chemical and physical characteristics of runoff water are expected to be highly variable. Temperature and concentrations of nitrogen and phosphorous nutrients have major impacts on microbial growth and degradation rates. Factors that may affect runoff water include seasonal variability and storm events.

The experiments were conducted using raw water from single samples and Mil-A-8243D aircraft deicer. The experimental results from this study may or may not be representative of degradation that would occur in water samples taken at different points in time. This

study does, however, highlight variables and conditions that are important when considering deicer degradation in the environment.

Caution should be exercised in applying lag times to situations in which oxygen depletion is a possibility. Degradation rates sufficient to cause oxygen depletion effects could be masked by analytical error. For example, 5% analytical error at 1000 mg/L propylene glycol is 50 mg/L with a corresponding oxygen requirement of roughly 50 mg/L. Over a two day sampling period, the oxygen demand would be 25 mg/L/day even though the degradation rate was not yet detectable.

J. Assessment of Potential Acute Environmental Impacts

1. Potential Oxygen Depletion

In most instances, the potential for oxygen depletion should be mitigated by environmental conditions. The lag phase provides time for dilution and dispersion to reduce concentrations of deicer components. Low temperatures and inadequate availability of nutrients reduce the potential for rapid biological degradation that might lead to oxygen depletion. However, the potential for oxygen depletion may be high in some situations. In phosphorous limited waters, the phosphate buffer in Mil-A-8243D aircraft deicer could provide sufficient phosphorous to promote rapid biological degradation that could deplete dissolved oxygen.

2. Aquatic Toxicity

The work of Pillard (9) and aquatic toxicity data for tolytriazole (2) have demonstrated the potential for aquatic toxicity of deicer additives. Since the potential for oxygen depletion will often be mitigated by environmental conditions as discussed above, aquatic toxicity will be the major acute effect of concern in most situations.

SECTION V
RECOMMENDATIONS

A. Information Needs

1. Runoff Characteristics

Additional information on deicer concentrations and nutrient levels in runoff would be useful in designing future experiments and in assessing the potential environmental impacts of aircraft deicers.

2. Deicer Formulations

The formulation of commercial deicers, particularly additives, is usually proprietary. Information on deicer composition is needed for evaluating potential environmental impacts and performing any needed research. For assessing deicer contributions to nitrogen and phosphorous requirements, either deicer composition or, at a minimum, the nitrogen and phosphorous contents are needed. Deicer composition is also needed for assessing aquatic toxicity and environmental fate of additives.

B. Recommendations for Further Work

Any additional information on runoff characteristics and deicer formulations should be included when considering future research.

1. Deicer Additives

Results of this study and the work of Pillard (9) indicate that aquatic toxicity is determined by deicer additives. Additional research, both in the lab and in the field, on the aquatic toxicity and environmental fates of the surfactant and flame retardant is indicated.

Potential reduction of phosphorous loadings by adsorption on soil and sediments should be evaluated. Reduction of phosphorous levels by partitioning to soil and sediment might reduce the impact of the phosphate buffer on phosphorous pollutant loadings and on degradation rates.

2. Laboratory Studies

Static flask experiments to assess the potential for oxygen depletion and anaerobic degradation should be considered in the design of future laboratory studies, whether conducted as research studies or as part of field or abatement design studies. The potential for oxygen depletion and anoxic/anaerobic degradation, when adequate supplies of nitrogen and phosphorous are available, was demonstrated in a static flask experiment. Mixing and reaeration in static flasks may be more representative of conditions in natural systems than conditions in shake flasks.

Addition of supplemental nitrogen and phosphorous as required to increase concentrations to mean concentrations expected in runoff from storm events should be considered in design of future lab experiments.

The temperature dependency determined in this study is not considered reliable due in part to uncertainty in degradation rates determined from batch experiments. Continuous stirred tank reactor (CSTR) experiments may be better suited to determining the temperature dependency of degradation rates. CSTR experiments could allow collection of multiple data points at each temperature and reduce the uncertainty in the determination of degradation rates.

Additional research on metabolites and intermediates of propylene glycol degradation may be warranted. Additional research in this area would be particularly indicated if difficulties are encountered in reducing BOD and COD to acceptable levels in treatment facilities. Aquatic toxicity testing will be a more effective method of addressing any toxicity concerns since it will be difficult or impossible to identify and quantify all metabolites and intermediates. Based on chromatographic peaks observed in this study and available information on metabolic pathways, aldehydes, ketones and organic acids should be targeted first.

3. Field Studies

The production of metabolites during environmental degradation of propylene glycol should be verified as part of field studies. The presence of metabolites can, potentially, be used as an indicator that biological degradation of propylene glycol is occurring. The presence of propionaldehyde and/or n-propanol, which are both easily detectable by gas chromatography, would indicate anaerobic degradation and oxygen depletion.

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